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Raman Spectra of Some Disubstituted Diacetylenes*

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Raman frequencies and relative intensities are reported for dimethyldiacetylene, diethyldiacetylene, dipropyldiacetylene, dibutyldiacetylene, and diamyldiacetylene. Depolarization factors also were obtained except for diethyldiacetylene. The relative intensities and depolarization factors were obtained with the use of a Gaertner microdensitometer. A tentative assignment was made of all the observed Raman frequencies of dimethyldiacetylene, assuming that it has the symmetry D'_{3h}. Using the chain and methyl group frequencies thus established for dimethyldiacetylene, a comparison was made with the other spectra in order to determine how these frequencies are affected by introducing additional CH_2 groups into the dimethyldiacetylene molecule. A comparison was made of the Raman spectra of the disubstituted diacetylenes with those of the corresponding acetylenes. For dimethyldiacetylene, three cases of Fermi resonance occurred, but there were also two cases where only a single line was observed, in spite of the fact that the frequency and symmetry conditions for resonance were satisfied. The carbon-carbon triple-bond frequency, which appears at 2183 cm^{-1} for diacetylene, increases to 2264 for dimethyldiacetylene, then drops to 2251–2257 for the other four compounds.

INTRODUCTION

PREVIOUS investigations in this laboratory and elsewhere have shown that disubstituted acetylenes generally have two or more lines near 2200 cm^{-1}. It seemed worth while to extend these investigations to see if the same behavior is exhibited by the disubstituted diacetylenes. Moreover, diacetylene itself has a very strong line at 2183 cm^{-1} which has been identified by Timm and Mecke[1] with the totally symmetrical frequency involving the carbon-carbon triple bond. If each of the hydrogen atoms of diacetylene is replaced with the same alkyl radical, one would expect this change to affect the above-mentioned frequency. Also since the Raman spectra of the corresponding disubstituted acetylenes have been obtained, a comparison of the spectra of the disubstituted acetylenes and diacetylenes should reveal information about the frequencies which may have a similar origin in the two types of compounds. The molecules selected were dimethyldiacetylene (2,4-hexadiyne), diethyldiacetylene (3,5-octadiyne), dipropyldiacetylene (4,6-decadiyne), dibutyldiacetylene (5,7-dodecadiyne), and diamyldiacetylene (6,8-tetradecadiyne). All of these compounds have the characteristic diacetylenic structure, $R-C\equiv C-C\equiv C-R$. No previous Raman or infra-red data could be found for any of the five compounds.

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[1] B. Timm and R. Mecke, Zeits. f. Physik **94**, 1 (1935).

TABLE I. Comparison of the Raman spectra of the disubstituted diacetylenes with the spectra of the corresponding acetylenes.*

Dimethyl-acetylene			Dimethyl-diacetylene			Diethyl-acetylene			Diethyl-diacetylene		Dipropyl-acetylene			Dipropyl-diacetylene			Dibutyl-acetylene			Dibutyl-diacetylene			Diamyl-acetylene			Diamyl-diacetylene		
$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ
									150	vw																		
213	VW					±206	6vb	0.8			(165)	(2b)					169	1b	0.8									
			±247	80	0.64																							
											342	1																
371	VVS	D				±364	3vb	0.7			±371	5	0.9				371	3					373	3	0.9			
																	389	3	0.6				383	1				
																	416	2	0.8									
																							435	1				
											468	2b	0.7	458	29					±467	45	0.86				468	38	0.48
			±475	220	0.64	484	1		479	10				±480	44	0.70	474	1b	0.7	±484	31	0.79				487	15	0.75
						499	3	0.7			(509)	(0)																
									521	4				526	6													
						532	2				534	0								540	4					539	4	0.86
											551	1					547	1b	0.7									
											578	1														(580)	vw	
			(686)	vw		681	2				674	2	0.9							(672)	vw					(675)	vw	
693	M	P				695	2																					
774	M	P				782	3	p	778	vw																		
																	803	3	0.7	803	6							
											808	3	0.4				811	4	0.4									
																										827	4	
											855	4	0.5	846	7	0.24							842	2	0.6			
																	873	3	0.6	866	vw							
											891	5	0.5	882	10	0.16							887	1	0.8			
																	901	3	0.6									
						918	2																					
																	929	2	0.7									
			(957)	vw					953	3							960	2	0.7	956	vw					(956)	vw	
																							970	1	0.9			
						983	7	0.3																				
																				(993)	vw							
1029	M	D	1020	vw							1020	1	0.9										1024	1	0.9			
											1037	2		1037	3													
																	1049	4	0.7	1048	7	0.27						
						1064	8	0.3	1063	5	1069	1	0.9										1067	3	0.8	1063	4	
											1095	4	0.5	1091	11	0.40												
																	1104	5	0.7	1101	11	0.64	1110	4	0.8	1104	10	0.19
																	1141	1										
			(1151)	vw																								
			(1185)	vw																								
						1207	½										1204	1										
																							1221	1		1219	8	0.40
			(1228)	vw					1231	6	1227	2	0.6	1228	10	0.47	1235	2	<0.7	1228	12	0.29						
			1253	17		1259	2	0.9	1254	vw	1260	3	0.6	1256	7	0.41												
											1274	1											1271	1				
											1291	1		1293	3		1295	3	0.8	1291	5	0.31	1300	3	0.9	1297	5	
						1319	7	0.6	1330	7	1327	5	0.6	1329	12	0.57	1326	4	0.6	1329	17		1330	3	0.9	1329	12	0.37
											1350	2	p	1347	9	0.61				1348	vw							
1380	S	P	1381	115	0.62	1376	2	p	1375	1																		
			1426	5		1439	5	0.7	1430	8	1434	5	0.8	1425	15	0.83	1440	5	0.8	1423	21	0.56	1436	6	0.8	1425	18	0.39
1448	MS	D	1458	vw		1460	4	0.8	1461	5	1456	4b	0.8	1452	10	0.55	1457	3b		1443	17	0.47	1452	3	0.8	1450	11	0.49
						2200	1	p									2195	0										
			2225	vw																								
2233	VS	P	2264	1000	0.40	2231	9	0.4	2257	1000	2234	10	0.5	2256	1000	0.33	2233	8	0.4	2251	1000	0.47	2231	7	0.4	2255	1000	0.19
						2247	8	0.4									2245	2	0.4				2248	2				
											2292	6	0.5				2296	5	0.4				2294	4	0.4			
2310	VS	P	2309	9		2301	6	0.4																				
			2502	vw																								
2737	MW					2729	2	p			2736	2	p				2729	1b	<0.9									
			2821	vw		2850	5	0.2	2836	12	2841	5	0.4	2830	10	0.22	2841	4	0.2	2827	13		2852	6		2827	vw	
2857	M		2848	21		2883	4	0.3	2884	28	2871	8	0.2	2869	48	0.26	2865	7		2864	58	0.16	2874	6	0.3	2861	44	0.20
2916	VS	P	2914	400	0.17	2909	10b	0.3	2913	59	2905	9	0.5	2904	81	0.35	2909	10	0.6	2902	110	0.30	2906	10	(0.6)	2900	93	0.27
						2939	10	0.1	2939	47	2936	9	0.4	2932	62	0.41	2931	8	0.1	2926	77	0.47	2934	8	0.1	2922	46	0.29
2966	MW		2954	39		2978	7	0.7	2982	25	2971	6	0.9	2966	21		2967	5	0.8	2957	23	0.69	2967	4	0.9	2956	vw	

* $\Delta\nu$ = Raman displacement in cm^{-1}, I = estimated relative intensity if intensity of strongest line is 10, but if intensity of strongest line is 1000 then I is the relative intensity measured with the densitometer, b = broad, vb = very broad, S = strong, VS = very strong, M = medium, MS = medium-strong, W = weak, MW = medium-weak, VW = very weak, vw = lines that were too weak to measure with the microdensitometer, ρ = depolarization factor ± indicates observation both as Stokes and anti-Stokes lines, parentheses enclose data in regard to which there is some question, D = depolarized ($\rho = 6/7$), P = polarized ($\rho \leq 6/7$), p means ρ was less than 6/7 but that it was not possible to make a quantitative measurement, and the brace joins lines that were unresolved on the polarization spectrogram. Data for dimethylacetylene were obtained from B. L. Crawford, Jr., J. Chem. Phys. **7**, 555 (1939); for diethylacetylene and dipropylacetylene from Forrest F. Cleveland, M. J. Murray, and H. J. Taufen, J. Chem. Phys. **10**, 172 (1942); for dibutylacetylene from M. J. Murray and Forrest F. Cleveland, J. Am. Chem. Soc. **63**, 1718 (1941), and for diamylacetylene from Forrest F. Cleveland and M. J. Murray, J. Am. Chem. Soc. **62**, 3185 (1940).

EXPERIMENTAL

Using the technique and apparatus described in previous papers,[2] spectrograms were obtained which were used to determine Raman frequencies, relative intensities, and depolarization factors. It was necessary to obtain some of the spectrograms with a fast Hilger E-518 spectrograph on account of the rapid decomposition of one of the samples. All of the samples were in the

[2] Forrest F. Cleveland, M. J. Murray, J. R. Coley, and V. I. Komarewsky, J. Chem. Phys. **10**, 18 (1942); Forrest F. Cleveland, J. Chem. Phys. **11**, 1 (1943).

TABLE II. A tentative assignment of the Raman frequencies of dimethyldiacetylene.*

Diacetylene			Dimethyldiacetylene				Dimethylacetylene			
Designation	$\Delta\nu$	Type of vibration	$\Delta\nu$	I	ρ	Assignment and symmetry	$\Delta\nu$	I	ρ	Assignment and symmetry
ν_9	230	deformation	247	80	0.64	Fund. E or $\bar{E}$				
ν_8	488	deformation	475	220	0.64	Fund. $\bar{E}$				
ν_3	644	C−C stretching	(686)	vw		Fund. A_1				
ν_1	(3350)	C−H stretching	(957)	vw		Fund. A_1				
			1020	vw		Fund. $\bar{E}$	1029	M	D	Fund. $\bar{E}$
			(1151)	vw		686+475=1161, $\bar{E}$				
			(1185)	vw		1442−247=1195, $\bar{A}_1+\bar{A}_2+\bar{E}$ or A_1+A_2+E				
			(1228)	vw		957+247=1204, E or $\bar{E}$				
			1253	17		1020+247=1267, $\bar{A}_1+\bar{A}_2+\bar{E}$ or A_1+A_2+E				
			1381	115	0.62	Fund. A_1	1380	S	P	Fund. A_1
			1426	5		Fund. 1442, $\bar{E}$	1448	MS	D	Fund. $\bar{E}$
			1458	vw		957+475=1432, $\bar{E}$				
			2225	vw		C^{13} isotope				
ν_2	2183	C≡C stretching	2264	1000	0.40	Fund. A_1				
			2309	9		957+1381=2338, A_1				
			2502	vw		2264+247=2511, E or $\bar{E}$				
			2821	vw		$1381^2=2762$, A_1	2737	MW		$1380^2=2760$, A_1
			2848	21		$1442^2=2884$, A_1+E	2857	M		$1448^2=2896$, A_1+E
			2914	400	0.17	Fund. A_1	2916	VS	P	Fund. A_1
			2954	39		Fund. $\bar{E}$	2966	MW		Fund. $\bar{E}$

* All symbols have the same meaning as in Table I with the exception of the braces which indicate probable cases of Fermi resonance.

liquid state with the exception of dimethyldiacetylene, which was put into solution in CCl_4. Excitation was by Hg 4358A. The intensities and depolarization factors were determined by use of a Gaertner microdensitometer as described elsewhere.[3] No polarization spectrogram could be obtained for diethyldiacetylene.

An outline of the method of preparation of the compounds is as follows:

Dimethyldiacetylene, C_6H_6: About 500 cm³ of liquid ammonia were placed in a 2-l, three-necked flask and 25 g of sodium were added in small pieces as acetylene was bubbled through the ammonia until the blue color of the solution disappeared.[4] The acetylene had been washed by passing through two bottles containing H_2SO_4 and then had been dried by passing over soda lime. A dry-ice acetone condenser was used.

After adding dropwise 130 g of $(CH_3)_2SO_4$, the mixture was allowed to stand ½ hr. Water was then added continuously and the gases evolved were passed through freshly prepared ammoniacal Cu_2Cl_2. When no more gas was evolved as water was added, the precipitated acetylide was filtered off using suction and washed until free of the blue color in the filtrate. It was then suspended along with the filter paper in 500 cm³ of water and 110 g of $K_3Fe(CN)_6$ were added.[5] The resulting mixture was steam distilled until no more product was obtained. The water was poured off the resulting white solid, $CH_3-C\equiv C-C\equiv C-CH_3$, which was then dissolved in CCl_4 and dried with Drierite. The solution was placed in a distilling flask and both CCl_4 and dimethyldiacetylene were distilled into the Raman tube in a partial vacuum.

The other compounds were prepared by the following method: The monosubstituted acetylene was obtained from acetylene, sodium, liquid ammonia, and the bromide of the radical being substituted for the hydrogen of the acetylene. The acetylenic Grignard reagent was formed in dry ether, using ethylmagnesium bromide. Using an ice bath, $CuBr_2$ was added slowly and with vigorous stirring to the acetylenic Grignard reagent.[6] When the reaction was complete, ice was added and the disubstituted diacetylene was

[3] Forrest F. Cleveland and M. J. Murray, J. Chem. Phys. 11, 450 (1943).

[4] Cf. T. H. Vaughn, G. F. Hennion, R. R. Vogt, and J. A. Nieuwland, J. Org. Chem. 2, 1 (1937).

[5] Cf. G. Griner, Ann. Chim. Phys. [6] 26, 354 (1892).

[6] James P. Danehy and J. A. Nieuwland, J. Am. Chem. Soc. 58, 1609 (1936).

then separated from the pasty mass by steam distillation. The boiling points of the compounds thus prepared were as follows:

Diethyldiacetylene, C_8H_{10},	77.5–80.0°C at 34 mm Hg,
Dipropyldiacetylene, $C_{10}H_{14}$,	76.0°C at 2 mm Hg,
Dibutyldiacetylene, $C_{12}H_{18}$,	97.0°C at 3 mm Hg,
Diamyldiacetylene, $C_{14}H_{22}$,	121.4°C at 2 mm Hg.

RESULTS

The experimental results for the disubstituted diacetylenes are listed in Table I. Also in Table I are given, for comparison purposes, the corresponding data for the disubstituted acetylenes, as reported by various observers. All the samples seemed to be fairly pure since no recognizable impurity lines were found in the Raman spectra, with the exception of diethyldiacetylene for which a very weak line was observed at 2179 cm^{-1}. This might indicate the presence of a trace of diacetylene as an impurity since diacetylene has its strongest line at 2183 cm^{-1}.

DISCUSSION

Probably the most outstanding characteristic of the Raman spectra of these disubstituted diacetylenes is the very strong line which appears for each compound in the 2250–2265 cm^{-1} region. Comparison with other molecules containing the acetylenic linkage indicates that this line is associated with the carbon-carbon triple-bond frequency. For diacetylene a similar line occurs at 2183 cm^{-1}. From Table I it appears that the greatest change in this frequency is produced when the two hydrogen atoms of diacetylene are replaced with methyl groups as this frequency has a greater value for dimethyldiacetylene than for any of the other diacetylenes investigated. Addition of CH_2 groups to the methyl groups which replace the hydrogen atoms does not seem to produce a greater shift, but results in a slight lowering of the Raman frequency, as observed for the other disubstituted diacetylenes. Furthermore, in all the disubstituted diacetylenes studied, with the exception of dimethyldiacetylene, only one line was observed in the 2200–2300 cm^{-1} region. This is somewhat different from the disubstituted acetylenes which usually have two or more lines in the same region.

Assuming that dimethyldiacetylene has the same symmetry as dimethylacetylene D'_{3h}, the tentative assignment of the Raman frequencies shown in Table II was made. The chain frequencies were established by comparison with Wu and Shen's[7] analysis of the vibrational spectrum of diacetylene. Crawford's[8] analysis of the dimethylacetylene Raman spectrum was used in determining the methyl group frequencies.

As a further aid in the analysis, the selection rules for fundamentals, binary combinations, overtones of non-degenerate frequencies, overtones of doubly degenerate frequencies up to the fourth overtone, for a molecule whose symmetry is D'_{3h}, and the number of frequencies of each type for dimethyldiacetylene, were obtained by methods described elsewhere.[9] The selection rules will not be listed here since they have already been published in a condensed form.[10] The selection rules allow five fundamental frequencies of type A_1, five of type E, and five of type $\bar{E}$ to appear in the Raman spectrum and four type $\bar{A}_2$ and the five E fundamentals to appear in the infra-red spectrum. The A_1 fundamentals should be polarized and the E and $\bar{E}$ frequencies should be depolarized. Unfortunately, no infra-red data were available and the tentative assignments therefore had to be based upon the Raman data alone. It is quite possible that these assignments may require revision if and when the infra-red data become available.

Without the calculated values of the fundamental frequencies it was not possible to give a unique assignment of the 247, 1185, 1228, 1253, and 2502 lines, since for these two assignments are possible depending upon whether the 247 fundamental is E or $\bar{E}$. However, it was possible to decide that the 475 cm^{-1} line was an $\bar{E}$ fundamental frequency in the following way: In order to have Fermi resonance between the $1442\bar{E}$ fundamental and the 1432 combination frequency, the symmetry condition requires[9] that the 1432 frequency have $\bar{E}$ symmetry. Since, according to the present assignment, 1432 cm^{-1} results from the combination of the $957A_1$ funda-

[7] T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (National University of Peking, Kunming, China, 1939), page 259.
[8] B. L. Crawford, Jr., J. Chem. Phys. **7**, 555 (1939).
[9] Arnold G. Meister, Forrest F. Cleveland, and M. J. Murray, Am. J. Phys. **11**, 239 (1943).
[10] Reference 7, page 296.

mental and the 475 fundamental, the 475 fundamental would have to be of $\bar{E}$ symmetry so that the combination frequency would have $\bar{E}$ symmetry. This is true because from the selection rules one sees that a combination of an A_1 frequency with an $\bar{E}$ frequency will have the symmetry $\bar{E}$.

Besides the case mentioned above, two other cases of Fermi resonance appear as shown in Table II. The first occurs between the $2264A_1$ fundamental and the 2309 combination frequency which results, according to the present assignment, from the combination of the 957 and $1381A_1$ fundamental frequencies. The other case appears to be more complicated, for now three frequencies seem to be interacting with one another; they are the first overtone of the $1381A_1$ fundamental, the first overtone of the $1442\bar{E}$ fundamental, and the $2914A_1$ fundamental.

Two other cases of Fermi resonance appear to be possible but were not observed. For example, the first overtone of the $475\bar{E}$ fundamental frequency would have the proper symmetry and energy level value to interact with the $957A_1$ fundamental. Yet in spite of this possibility no other line was observed in this region. However, the 957 cm^{-1} fundamental was quite weak and it is possible that the resonance component might have escaped observation. Another possible case of resonance which was not observed could occur between the first overtone of the $686A_1$ fundamental and the $1381A_1$ fundamental, since both the overtone and the fundamental frequency would have the same symmetry, A_1, and $686^2 = 1372$.

If one assigns the line at 1185 cm^{-1} to the difference tone (1442 − 247), one would expect a line to appear at (1442 + 247) = 1689 cm^{-1}, for according to Herzberg,[11] if a difference tone is present, the corresponding summation frequency, since it is undiminished by a Boltzmann factor, should appear with even greater intensity. Also, for the same reason, if the line at 2225 cm^{-1} is assigned to the (2914 − 686) difference tone, one would expect a line to be found at (2914 + 686) = 3600 cm^{-1}. Yet in neither of these cases were lines observed in the Raman spectrum. In view of this difficulty, it seems better to assign the 2225 cm^{-1} line to the triple-bond frequency of an isotopic molecule containing C^{13}. Another alternative might be that dimethylacetylene was present as an impurity. Since this compound has very strong lines at 2233 and 2310 cm^{-1}, the lines at 2225 and 2309 cm^{-1} could indicate the presence of a trace of dimethylacetylene, although this seems improbable in view of the method of preparation.

A study of Table II indicates that of the fifteen fundamental frequencies which are permitted in the Raman effect, only ten have been given an assignment. All five A_1 fundamental frequencies seem to have been observed, but only four or possibly five of the $\bar{E}$ fundamental frequencies were observed, depending on the final assignment of the 247 cm^{-1} line which tentatively has been assigned to an E or $\bar{E}$ fundamental. For the same reason only one or none of the five E frequencies was observed. This same scarcity of E fundamentals was observed by Crawford[8] in his analysis of the Raman spectrum of dimethylacetylene; of the four E-type fundamental frequencies which were allowed in the Raman spectrum, only one was observed. Since for this compound all of the missing E fundamentals were observed in the infra-red spectrum, one would expect that if the infra-red spectrum of dimethyldiacetylene were obtained, it would help to determine the missing E-type fundamental frequencies. Of course, it is possible that some of the frequencies did not occur in the Raman spectrum because they lie too close to other frequencies and were thus not resolved, or else because the lines while they are permitted by the selection rules were too weak to be observed.

From Table I, it is possible to get a good indication of the behavior of the chain frequencies as CH_2 groups are added to the dimethyldiacetylene molecule. The 247 cm^{-1} E or $\bar{E}$ fundamental of dimethyldiacetylene either was not observed for the other disubstituted diacetylenes or else its value was changed considerably, as the other compounds have no line near this value. On the other hand, the 475 cm^{-1} $\bar{E}$ fundamental frequency seemed to increase slightly as more CH_2 groups were added, each compound having a line in the 475–490 cm^{-1} region with diamyl-

[11] G. Herzberg, private communication.

diacetylene having the greatest frequency value. In contrast to this behavior the 686 A_1 fundamental frequency seemed to decrease slightly, but whether the decrease is significant is hard to say since this frequency was not observed in the spectra of two of the disubstituted diacetylenes. The 957 cm^{-1} A_1 fundamental was observed in only three of the other compounds and was not very strong in any of the four cases. Finally, the 2264 cm^{-1} A_1 fundamental appears to be affected very little since its value for the other four compounds lies between 2251–2257 cm^{-1}.

In a similar manner one can observe the behavior of the methyl group frequencies. The 1020 cm^{-1} $\bar{E}$ fundamental seems to be changed considerably or else was not observed in some cases since only two compounds had lines which were found near this value. A similar behavior is shown by the 1381 cm^{-1} A_1 fundamental since diethyldiacetylene was the only compound which had a line near this value. The 1442 cm^{-1} $\bar{E}$ frequency seems to be present in all the compounds, although its value seems to change rather sporadically from one compound to another. A similar behavior is exhibited by the 2914 cm^{-1} A_1 fundamental since it is found for all the compounds in the 2922–2939 cm^{-1} region. The line lying in this region has been chosen as corresponding to the A_1 fundamental rather than the line which appears for all the compounds in the 2900–2913 region, because if one compares the ratio of the intensity of the line in the 2900–2913 region to the intensity of the line in the 2922–2939 region, one finds that the ratio increases as the number of CH_2 groups increases, having its greatest value for diamyldiacetylene. So the line in the 2900–2913 cm^{-1} region is believed to be associated with the CH_2 groups while the line in the 2922–2939 cm^{-1} region is associated with the methyl group. Furthermore, it has been shown[12] that the methyl group usually has a polarized frequency in the 2930 cm^{-1} region, so it seems more reasonable to associate the line in this region with the polarized frequency of the methyl group. All that remains is the 2954 cm^{-1} $\bar{E}$ fundamental frequency which seems to be present in all of the compounds; its value changes considerably from compound to compound at first but for the last two compounds in the table is about the same. This frequency has its greatest value for diethyldiacetylene.

ACKNOWLEDGMENTS

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[12] Forrest F. Cleveland, M. J. Murray, H. H. Haney, and Julia Schakelford, J. Chem. Phys. **8**, 153 (1940); Forrest F. Cleveland and M. J. Murray, J. Am. Chem. Soc. **62**, 3185 (1940).

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Dissociation of Methyl Chloride on a Hot Filament*

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An experimental method for determining directly the bond energies in some polyatomic molecules is suggested, and the experimental data obtained in applying it to the case of carbon-chlorine bond in methyl chloride are presented and discussed. The decomposition of methyl chloride and carbon tetrachloride on hot tungsten is shown to be quite inefficient.

INTRODUCTION

THE bond energy in the case of diatomic molecules has a unique value for it is simply the dissociation energy at absolute zero. For practically all such bond energies spectroscopists have catalogued precise values. Proceeding to the case of polyatomic molecules, the meaning of bond energy becomes less definite. If a polyatomic molecule contains only two atomic species the bond energy could be defined as being equal to the atomic heat of formation divided by the number of bonds in the molecule. For example, the energy necessary to split an H_2O molecule into one O atom and two H atoms in the ground state is 218.9 kcal. and the O—H bond energy may be assigned a value of 109.5 kcal. It is well known that this value deviates considerably from the true separation energies since 119.5 kcal. are required to remove the first hydrogen from water and 99.4 kcal. to separate the O—H radical.[1] When a polyatomic molecule composed of more than two atomic species is considered, an individual bond energy is usually regarded as the energy of separation of the two parts united by the bond in question; and, indeed, this seems to be almost the only rigorously definable quantity which can be used to fit the general concept.

One must distinguish between bond energy and activation energy. The latter may be larger than, but can never be smaller than, the bond energy. The bond energy we shall take to be the energy difference between the normal molecule in the ground level and the two separated atoms or radicals in their ground level. This is the energy of the gaseous reaction at 0°K. In only a very few cases is it possible to determine directly the energy required to separate an atom or a radical from a polyatomic molecule. The desire to measure directly this energy of separation in polyatomic molecules led to work reported here.

OUTLINE OF THE METHOD

In some experiments concerned with measuring electron affinities it has been shown that hydrogen,[2] chlorine,[3] and bromine[4] molecules come to complete thermal equilibrium when they collide with a hot tungsten surface. This is described by stating that the accommodation coefficient for these gases on hot tungsten is unity. In the case of chlorine, for example, all the chlorine molecules hitting the tungsten wire (about 2000°K) would decompose into atoms whereupon the reaction

$$Cl + e \rightarrow Cl^- \qquad (1)$$

would occur. By a suitable experimental arrangement it was possible to measure the concentration of Cl and the ratio of chloride ions to electrons. This permitted the calculation of the equilibrium constant and hence the energy (electron affinity) of the above reaction. Incidentally, the fraction of chloride ions in the equilibrium mixture is very small. It was noted in these experiments that stannic chloride also exhibited an accommodation coefficient of unity. In view of this it was hoped that if methyl chloride were passed

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.
** Present Address: Polytechnic Institute of Brooklyn, Brooklyn, New York.
[1] O. Riechmeier, H. Steuftteben, and H. Pastorff, Ann. d. Physik **19**, 202 (1934).
[2] P. M. Doty, J. Chem. Phys. **11**, 557 (1943).
[3] K. J. McCallum and J. E. Mayer, J. Chem. Phys. **11**, 56 (1943).
[4] P. M. Doty and J. E. Mayer, J. Chem. Phys. **12**, 323 (1944).

over a hot tungsten filament at low pressure the reaction

$$CH_3Cl \rightarrow CH_3 + Cl \qquad (2)$$

would occur on the surface, with an accommodation coefficient of unity, followed by reaction (1). This would allow a determination of the carbon-chlorine bond energy in methyl chloride as follows.

From the measured electron affinity of chlorine (negative of the energy change) one calculates the equilibrium constant K_1, of reaction (1) over the desired temperature range. Using this relation the pressure of the chlorine atoms on the tungsten surface may be expressed as

$$P_{Cl} = \frac{1}{K_I} \frac{P_{Cl^-}}{P_e}. \qquad (3)$$

The experimental arrangement allows the measurement of the ratio of the chlorine ions to electrons, Z_{Cl^-}/Z_e, leaving the filament. Relating this ratio to the pressures of the species by the Langmuir-Knudsen equation changes Eq. (3) into

$$P_{Cl}(\text{atmos.}) = \frac{1}{K_I}\left(\frac{M_{Cl^-}}{M_e}\right)^{\frac{1}{2}} \frac{Z_{Cl^-}}{Z_{e^-}} = 254 \frac{Z_{Cl^-}}{Z_e} \frac{1}{K_I}. \qquad (4)$$

If we equate the pressure of the chlorine atoms to the pressure of the methyl radicals and use the measured pressure of methyl chloride, the equilibrium constant K_{II} for reaction (2) may be evaluated. Measuring the equilibrium constant in this way at various temperatures gives data from which the equilibrium constant of reaction (2), the bond energy, may be calculated. This procedure should in general lead to the determination of bond energies for any covalent bond formed by the halogens or oxygen since the electron affinity of these atoms has been determined by the method described.

The accommodation coefficient would have to be unity in order to evaluate reliably the bond energy by this method. In carrying out the experimental work with methyl chloride it soon became apparent, as explained later, that the accommodation coefficient of methyl chloride was far less than unity. The method of this particular application would then appear to break down; therefore, it seems at first remarkable to find that a plot of log $K_{I(expt)}$ *versus* $1/T$ is a straight line whose slope yields a reasonable value for the carbon-chlorine bond energy.

TABLE I.

Temp. °K	Pressure (microns)	Z_{Cl^-}/Z_e	K_{II}	P_{Cl}(atmos)	$K_{I(expt)}$
1561	10.0	0.327	35.1×10^{8}	2.72×10^{-8}	0.423×10^{-10}
1592	10.0	0.256	19.1	3.40	0.879
1630	12.3	0.185	9.55	4.93	1.50
1722	9.6	0.200	2.00	2.54	5.10
1848	11.1	0.0654	0.295	5.63	20.9
1921	11.6	0.369	0.109	8.60	48.5

EXPERIMENTAL RESULTS

The apparatus used in the research has been described[4] in a previous publication. In brief, the apparatus consists of a tungsten filament so arranged that methyl chloride at any constant low pressure may pass over the electrically heated filament. Concentric with the filament are, in order, a radial grid, a plate (collector) connected to an FP-54 Dubridge amplifier, and then, outside of the vacuum system, a solenoid. With proper positive potentials electrons and chloride ions go to the plate where they register on the galvanometer attached to the output of the amplifier. When the solenoid is activated the electrons are turned into the grid and the ion current alone is measured. The temperature of the filament is determined by its resistance found by measuring the current and voltage across the filament. A McLeod gauge is used to determine the pressure of methyl chloride.

In Table I the experimental data for methyl chloride are recorded. In the last column of the table is listed the value of

$$\frac{P_{Cl}P_{CH_3}}{P_{CH_3Cl}} = \frac{P_{Cl}^2}{P_{CH_3Cl}} = K_{I(expt)} \qquad (5)$$

in units of atmospheres.

The plot of log $K_{I(expt)}$ *versus* reciprocal absolute temperature as shown in Fig. 1 is a reasonably straight line with a slope corresponding to 74 kcal. per mole. This may be compared with 66.5[5] and 73[6] kcal. per mole, often quoted values of carbon-chlorine bond energy.

[5] O. K. Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Company, Inc., New York, 1940).

[6] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, 1941).

Carbon tetrachloride was then used in the apparatus to compare its behavior with that of methyl chloride and stannic chloride. Several measurements were taken at 1560°K and 10 microns pressure. The results of these measurements showed that under the above conditions the ratio of carbon tetrachloride molecules hitting the hot surface to the chlorine atoms formed was about 160. From Fig. 1 the corresponding ratio for methyl chloride at the same temperature and pressure is 920. This indicates that the carbon-chlorine bond in carbon tetrachloride is either weaker than it is in methyl chloride or that the accommodation coefficient is greater than in methyl chloride although it is still far from unity.

EFFICIENCY OF THE METHYL CHLORIDE DECOMPOSITION

The incomplete attainment of thermal equilibrium by methyl chloride on hot tungsten is clearly demonstrated by calculating the equilibrium constant for reaction (1) at 1560°K and comparing it with $K_{I(expt)}$. This step requires the calculation of ΔS for reaction (1)—a calculation that can be done with moderate accuracy. The entropy of methyl chloride is given by Stevenson and Beach[7] at 800°, 1000°, and 1200° from which it is easy to extrapolate to 1560°. From the work of Penney[8] and VanVleck[9] it follows that the methyl radical is a planer structure and the frequency assignment, 2850, 3182 (2), 1065, 1383 (2), was obtained by extrapolation methods using the corresponding frequencies of the methyl halides.[9] Using this together with the entropy of the chlorine atom the entropy change at 1560° is found to be 42.3 e.u. This is then used in the relation $-RT \ln K = \Delta H - T\Delta S$ to obtain for K_I at 1560° a value of 0.076. When this is compared with the value of $K_{I(expt)}$ from Table I, it is apparent that the accommodation coefficient is far less than unity. In other words, this calculated equilibrium constant predicts that out of 1000 methyl chloride molecules hitting the hot filament (1560°K) 987 are decomposed according to Eq. (1), whereas actually only about 1 molecule decomposes out of the thousand.

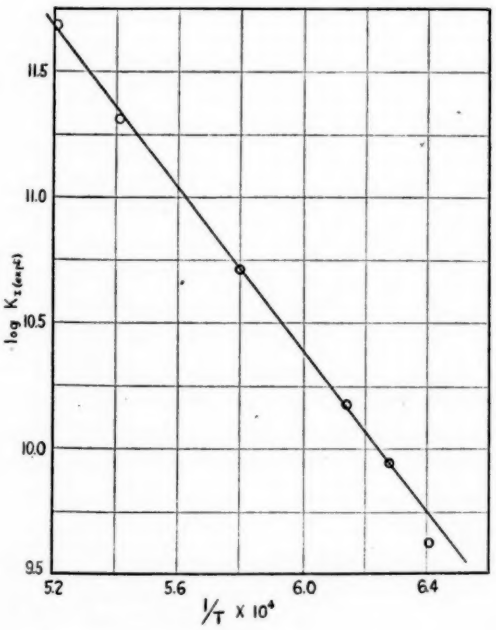

FIG. 1.

CONCLUSION

An experimental method for determining directly the bond energies in some polyatomic molecules has been discussed and the experimental data obtained in the first attempt to apply the method have been presented. The method cannot be applied with certainty and simplicity unless it can be demonstrated that the molecule being investigated comes to thermal equilibrium on a hot filament. This could be shown either by measuring the energy loss of the filament which should equal the energy used in breaking the bonds plus additional translational energy or by determining at higher temperatures the electron affinity of the halogen contained in the compound.

In the case investigated here it is shown that the methyl chloride does not come to equilibrium; yet, by calculating a quasi-equilibrium constant for the decomposition, a reasonable value for the carbon-chlorine bond energy is obtained. This situation is consistent with the kinetic picture that the energy of adsorption of methyl chloride on the hot surface (probably carbon coated) is negligibly small and that only methyl chloride molecules colliding with the

[7] D. P. Stevenson and J. Y. Beach, J. Chem. Phys. 6, 25 (1938).
[8] W. G. Penney, Trans. Faraday Soc. 31, 734 (1935).
[9] J. H. VanVleck, J. Chem. Phys. 1, 219 (1933).

filament at a particularly favorable orientation come to thermal equilibrium with the surface. A small constant accommodation coefficient would follow from this. The postulated circumstances are reminiscent of the interpretation of the hydrogen molecule-hydrogen atom exchange reaction where the hydrogen atom must meet the hydrogen molecule close to the line of centers for a reaction to be effected.[10]

The author is deeply indebted to Professor Joseph E. Mayer who suggested this problem and continually guided its progress.

[10] J. O. Hirschfelder, H. Eyring, and B. Topley, J. Chem. Phys. **4**, 170 (1936).

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Equilibrium Distribution in Sizes for Linear Polymer Molecules

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Systems of linear polymer molecules are characterized by favorable heats of polymerization counterbalanced by unfavorable entropies of polymerization. Long chains are therefore formed and are stable at low temperatures while at sufficiently high temperature appreciable amounts of monomeric units split off. At any given temperature there exists a definite equilibrium distribution in sizes. This distribution is derived here by statistical methods and proves to be a very simple function of the heat of polymerization.

POLYMERIC materials occurring in nature or produced in the laboratory display a distribution in molecular sizes. The so-called molecular weight distribution curves have been rather intensively investigated in recent years from both the experimental and theoretical viewpoints.

The theoretical studies have been based on statistical or kinetic treatments of the postulated mechanism of formation of the polymers. For example, Flory[1] developed the theory for size distribution in condensation polymers by a statistical treatment. Kuhn,[2] Mark and Simha,[3] Montroll,[4] and others developed the theory for size distributions resulting from chain degradation. Flory[5] and Stockmayer[6] have investigated the theory of size distribution in branched polymers. Several authors[7–9] have discussed size distributions resulting from postulated chain mechanisms of polymerization by integrating the kinetic equations.

There have been, however, few attempts to discuss quantitatively the equilibrium distribution that must exist between polymerized and unpolymerized material as a function of temperature. It has generally been tacitly assumed that in a certain temperature range polymers will keep growing in size, restricted only by the kinetic situation, until all the monomer and short polymers are incorporated into one giant molecule.

It is, however, well known that polymers, such as polystyrene and many other chain polymers, will break down at high temperatures and give a large percentage of monomeric material. It is also known that polymers formed at high temperatures generally have a lower average molec-

[1] P. J. Flory, J. Am. Chem. Soc. **58**, 1877 (1936).
[2] W. Kuhn, Ber. **B63**, 1503 (1930).
[3] H. Mark and R. Simha, Trans. Faraday Soc. **36**, 611 (1940).
[4] E. W. Montroll and R. Simha, J. Chem. Phys. **8**, 721 (1940).
[5] P. J. Flory, J. Am. Chem. Soc. **63**, 3083, 3091, 3096 (1941).
[6] W. H. Stockmayer, J. Chem. Phys. **11**, 45 (1943); *ibid.* **12**, 125 (1944).
[7] G. V. Schulz, Zeits. f. physik. Chemie **B32**, 27 (1936); *ibid.* **B43**, 25 (1939).
[8] E. F. Herrington and A. Robertson, Trans. Faraday Soc. **38**, 490 (1942).
[9] Hulbert, Harmon, Tobolsky, and Eyring, Ann. N. Y. Acad. Sci. **44**, 371 (1943).

ular weight than those formed at low temperatures.* All polymerizations are exothermic, the heat of polymerization in vinyl polymerizations being generally of the order of 10–20 kcal. per mole of monomer. The favorable heat of polymerization is counterbalanced by an unfavorable entropy of polymerization. It is, therefore, to be expected that high temperatures would tend to favor depolymerization, whereas at low temperatures large polymeric molecules would be stable. At any given temperature, however, there should be an equilibrium distribution in sizes, corresponding to a condition where entropy and heat are balanced so as to give a minimum free energy.

An attempt to obtain the equilibria obtaining among chains of all sizes in polymeric sulfur was made by Powell and Eyring.[10] These authors used empirical expressions for the entropy of polymerization, but were able to explain many of the observed phenomena pertaining to "elastic sulphur" by means of their equations. A treatment of random reorganization in linear condensation polymers was made by Flory.[11]

The basis for a more general theory of the equilibrium distribution in sizes for linear chain polymers is inherent in papers by Flory[12] and by Huggins[13] on the entropy of randomness of a mixture of solvent and polymer molecules. The method used by these authors is to construct a lattice upon whose sites solvent molecules or segments of the long chain polymers can be moved interchangeably, and to count the number of available distinct configurations. From this work in conjunction with a recent note by Flory[14] it can easily be inferred that the logarithm of the number of configurations Ω available to a mixture of n_0 solvent molecules and n_1 molecules of monomer, n_2 molecules of dimer, n_x molecules of x-mer, etc., is

$$\ln \Omega = -\sum_{x=1} n_x \ln \frac{n_x}{n_0+\sum xn_x} - n_0 \ln \frac{n_0}{n_0+\sum xn_x} + \sum_{x=1} (x-1)n_x[\ln(\gamma-1)-1] - \sum n_x \ln \sigma, \quad (1)$$

where γ is the coordination number of the lattice and σ is the symmetry number of the long chain molecule (usually 2).

THE EQUILIBRIUM DISTRIBUTION

If the distribution of polymer sizes is known (by specification of the n_x's), Eq. (1) gives the number of available configurations. The energy of each distribution with specified values of the n_x's can easily be written in terms of the heat of polymerization per molecule, P.†

$$E = -\sum n_x(x-1)P. \quad (2)$$

The equilibrium properties of a system containing n_0 solvent molecules and N monomeric units (which may be linked together in any fashion into polymeric units) can be obtained in theory by evaluation of the partition function.

$$Z = \sum_i \Omega_i \exp\{-E_i/kT\} \quad (3)$$

where the subscript i refers to a particular set of the n_x's corresponding to a definite distribution in sizes among the polymer molecules.

Each term in the summation corresponding to any combination n_1, n_2, n_3, etc., consistent with condition (5) below corresponds to a macrostate of the system. The macrostate corresponding to "equilibrium" is the state for which the free energy is a minimum and can be found by maximizing the expression.

$$\ln \Omega_i - E_i/kT \quad (4)$$

with respect to the variables n_1, $n_2 \cdots n_x$, $\cdots$ subject to the condition that

$$\sum_{x=1} xn_x = N. \quad (5)$$

The problem of maximizing (4) subject to (5) can be best solved by the method of Lagrange multipliers. In other words, multiply Eq. (5) by $-\alpha/kT$ and add to Eq. (4) giving, after sub-

* Although this may in part be due to the different temperature coefficients of the rate constants involved in the kinetic mechanism, there is evidence that indicates that the molecular weights at temperatures of 130°C and above are definitely delimited by polymerization-depolymerization equilibria.

[10] R. Powell and H. Eyring, J. Am. Chem. Soc. **65**, 648 (1943).

[11] P. J. Flory, J. Am. Chem. Soc. **64**, 2205 (1942).

[12] P. J. Flory, J. Chem. Phys. **10**, 51 (1942).

[13] M. L. Huggins, J. Phys. Chem. **46**, 151 (1942).

[14] P. J. Flory, J. Chem. Phys. **12**, 114 (1944). A similar but more detailed treatment has been made by R. Scott and M. Magat (soon to be published).

† Consideration of the vibrational entropy of the lattice model is omitted as being of secondary importance.

stituting Eq. (1),

$$\phi=\sum_{x=1} n_x\frac{(x-1)P}{kT}-\sum_{x=1} n_x \ln\frac{n_x}{n_0+\sum xn_x}$$
$$-n_0\ln\frac{n_0}{n_0+\sum xn_x}$$
$$+\sum_{x=1}(x-1)n_x[\ln(\gamma-1)-1]$$
$$-\sum n_x\ln\sigma-\frac{\alpha}{kT}\sum xn_x. \quad (6)$$

Differentiating ϕ with respect to each of the n_x's and setting these derivatives equal to zero, the following expression is obtained upon solving for $\ln\dfrac{n_x}{n_0+\sum xn_x}$:

$$\ln\frac{n_x}{n_0+\sum xn_x}=\frac{x-1}{kT}P-v_p\left(1-\frac{x}{\bar{x}_n}\right)$$
$$+(x-1)(1-v_p)-\ln\sigma$$
$$+(x-1)[\ln(\gamma-1)-1]+\frac{\alpha x}{kT}, \quad (7)$$

$x=1, 2, 3, \cdots$, where

$$v_p=\frac{\sum_{x=1} xn_x}{n_0+\sum_{x=1} xn_x}, \quad (8)$$

and

$$\bar{x}_n=\frac{\sum_{x=1} xn_x}{\sum_{x=1} n_x}. \quad (9)$$

From Eq. (7) the following is immediately derived:

$$\frac{xn_x}{n_0+\sum xn_x}=x\exp\left\{\frac{(x-1)}{kT}P+\frac{\alpha x}{kT}\right.$$
$$-v_p\left(1-\frac{x}{\bar{x}_n}\right)+(x-1)(1-v_p)$$
$$\left.-\ln\sigma+(x-1)[\ln(\gamma-1)-1]\right\}$$
$$=\left(\frac{x}{\beta}\right)\exp x\left[\frac{P}{kT}+\frac{\alpha}{kT}+\frac{v_p}{\bar{x}_n}-v_p+\ln(\gamma-1)\right]$$
$$=\left(\frac{x}{\beta}\right)y^x e^{-P/kT}, \quad (10)$$

where

$$y=\exp\left\{\frac{P}{kT}+\frac{\alpha}{kT}+\frac{v_p}{\bar{x}_n}-v_p+\ln(\gamma-1)\right\}, \quad (11)$$

and

$$\beta=\sigma(\gamma-1). \quad (12)$$

The value of α must be obtained by summing Eq. (10) over all values of x and setting the result equal to v_p. This operation leads to the following equation

$$\frac{y}{(1-y)^2}=v_p\beta e^{P/kT}. \quad (13)$$

Solution of the quadratic equation for y leads to the following:

$$y=1+\frac{1}{2(v_p\beta e^{P/kT})}$$
$$-\frac{1}{2}\left[\frac{4}{v_p\beta e^{P/kT}}+\frac{1}{(v_p\beta e^{P/kT})^2}\right]^{\frac{1}{2}}. \quad (14)$$

Upon substituting Eq. (14) in (10) an exact expression for the equilibrium size distribution is obtained. A normalized approximate result (based on the assumption that $e^{P/kT}\gg 1$) is:

$$\frac{\dfrac{xn_x}{n_0+\sum xn_x}}{v_p}=x\frac{1}{\beta v_p e^{P/kT}}\left(1-\frac{1}{(\beta v_p e^{P/kT})^{\frac{1}{2}}}\right)^{x-1}. \quad (15)$$

The distribution in sizes for polymer molecules at equilibrium thus obtained is of the same form as distributions previously derived by statistical treatments for the formation of linear condensation polymers or for the degradation of "infinite" linear polymers. The latter is particularly easy to visualize: If an infinite polymer is degraded by a random scission process, and the probability that *any* given bond is cut is p, then the weight fraction of x-mer is

$$W(x)=xp^2(1-p)^{x-1}. \quad (16)$$

Comparing (16) with (15) we see that the equilibrium distribution can be considered to be the result of a random scission process on an "infinite" linear polymer, the probability of scission at any temperature being equal to

$$p=\frac{1}{(\beta v_p e^{P/kT})^{\frac{1}{2}}}. \quad (17)$$

Butene-1 and Butene-2 Equilibrium

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The equilibrium between butene-1 and butene-2 was attained on activated alumina at 400 and 450°C. The values obtained were found to agree with calculated results.

ISOMERIZATION of butenes has been studied using a variety of catalysts such as phosphoric acid, perchloric acid, $C_6H_5SO_3H$, and zinc chloride solutions.[1] Others have used floridin, aluminum sulfate, phosphoric acid on charcoal, and various clays[2] resulting in isobutene production from *n*-butenes.

Some controversy has arisen as to the products of this isomerization and in the related subject of dehydration of *n*-butanol employing activated alumina as the catalyst. Fourneau and Puyal[3] using infusorial earths and clays obtained practically 100 percent butene-2 on dehydrating *n*-butanol. Davis[4] dehydrated the straight chain alcohol over alumina in the temperature range 340–360°C to get 35 percent butene-2 and 65 percent butene-1. His method of analysis involved relative rates of bromination of the two

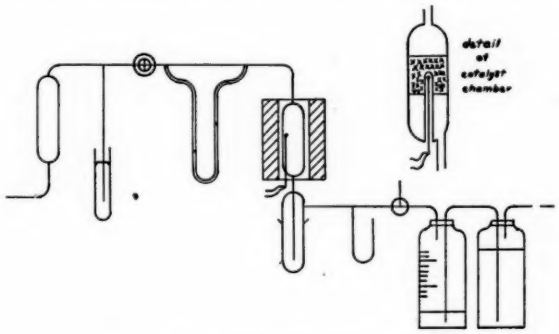

FIG. 1. Gas flow system.

isomers. Lucas, Dillon, and Young[5] developed a method of analyzing mixtures of the brom butenes by fractional distillation under reduced pressure to minimize the possible thermal isomerization of the brom derivatives. These brom butenes were then reacted with KI to regenerate the butene and iodine. Since the second-order reaction rates of the three normal brom butenes (-1, -2 *cis* and *trans*) differ, a method of analysis was possible, in combination with physical measurements such as refractive indexes and densities. This tedious method was then applied in a study of the dehydration of butanols over various catalysts including alumina.[6] In a temperature range 335–370°C they obtained from butanol-1, 27 percent butene-2 (*cis* and *trans*) and from butanol-2, 79 percent butene-2. The yields of butene-2 from butanol-1 were much lower than those obtained with acidic catalysts such as sulfuric acid or P_2O_5. Pines[7] dehydrated butanol over "Alorco" activated alumina at 375–425°C to form essentially butene-1. Fractional distillation in a Podbielniak precision apparatus was employed in analysis. Pines points out that the fractional distillation of dibrom derivatives can result in isomerization thus rendering such a method questionable. Ipatieff[1] and co-workers and Le Pingle[8] substantiate these results. Not a single case of production of isobutene in these isomerization and dehydration studies using alumina catalysts was reported.

Matignan, Moreau, and Dode[9] explained the variance in results as due to trace acidic constituents such as sulfate ion in the catalyst. Alumina prepared from sulfate free aluminum hydroxide gave butene-1 on dehydration of the *n*-alcohol, whereas introduction of a small amount of sulfate or nitrate resulted in high yields of butene-2. Their method of analysis

[1] Ipatieff, Pines, and Schaad, J. Am. Chem. Soc. **56**, 2696 (1934).
[2] Frost, Rudkovskij, and Serebrajakova, Comptes rendus (Doklady) Acad. Sci. U.S.S.R., [13] **4**, 373 (1936).
[3] E. Fourneau and J. Puyal, Bull. Soc. Chim. **31**, 424 (1922).
[4] Davis, J. Am. Chem. Soc. **50**, 2769 (1928).
[5] H. J. Lucas, R. T. Dillon, and W. G. Young, J. Am. Chem. Soc. **52**, 1949–52; 1953–64 (1930).
[6] W. G. Young and H. J. Lucas, J. Am. Chem. Soc. **52**, 1964 (1930).
[7] H. Pines, J. Am. Chem. Soc. **55**, 3892 (1933).
[8] M. Le Pingle, Bull. Soc. Chim. **39**, 741 (1926).
[9] Matignan, Moreau, and Dode, Bull. Soc. Chim. [5] **2**, 1169–81; 1181–88 (1935).

involved a study of distillation curves characteristic of mixtures of the dibrom derivatives. For quantitative results preparation of the diacetates and glycol derivatives was necessary with subsequent oxidation to diacetyl, treatment with hydroxylamine to form dimethyl glyoxime, and precipitation as the nickel complex.

In the present work a study of the isomerization of butene-1 to butene-2 and vice versa was conducted at 400 and 450°C over a range of contact times 2–65 seconds. Infra-red absorption spectrum measurements were employed as the method of analysis. Activated alumina was used in this study to remove the complicating factor of possible isomerization to isobutene. In the temperature range 400–450°C equilibrium could be approached from both sides in quite short contact times.

MATERIALS

Tank butene-1 and butene-2 were obtained from the Matheson Company, East Rutherford, New Jersey. They were used without further purification other than drying. Vapor pressure measurements indicated pure butene-1, and a butene-2 consisting of a 70 percent *cis*, 30 percent *trans* mixture. Ten cc of "Alorco" activated alumina (Grade A, 8–14 mesh) was heated slowly in a stream of air to 450°C and was then ready for use.

APPARATUS

All experiments were performed in a simple flow system (see Fig. 1). The gases were fed from the tank and dried by passing through a calcium chloride tube. A Ventille valve served as flow regulator. Rates of flow were read from a calibrated flowmeter. The catayltic chamber was encased in an electrically heated furnace. The chamber's construction permitted preheating of the gases followed by contact with the 10-cc catalyst. A Chromel-Alumel thermocouple embedded in the catalytic mass recorded the temperature by a direct reading pyrometer. Product gases were collected in a calibrated one-liter gas bottle. The entire run product was then transferred to an apparatus which enabled small samples to be cooled to liquid air temperature, residual gases pumped off, and transferred to sample tubes ready for analysis. The catalyst was flushed with nitrogen and air passed through the mass at 450°C after each run.

ANALYSIS

The intensity of the 5.45-μ band of butene-1 was used as the basis of analysis. The details will be given in a later work.[10] Butene-2 was found to contain no such band. No attempt was made to analyze for *cis*- and *trans*-butene-2. Mixtures of the two olefins of known composition were measured at this wave-length and a calibration curve was obtained, plotting I/I_0 values against percent butene-1. The result of one run was checked by vapor pressure measurements and was found to agree with this method extremely well.

RESULTS

At 450°C the results were as shown in Table I.

The accompanying diagram (Fig. 2) summarizing these results shows graphically the approach to equilibrium from both sides at the two temperatures considered. With long contact

TABLE I.

Run No.	Percent butenes -1	-2	Contact time, sec.	Vol. of run, cc	Butene used
B-39	39.0	61.0	7.1	1000	1
-40	39.0	61.0	7.2	600	1
-41	35.0	65.0	10.9	600	1
-42	50.5	49.5	2.1	800	1
-45	23.5	76.5	7.8	700	2
-46	18.0	82.0	1.9	650	2
-47	23.5	76.5	11.8	725	2
-48	21.0	79.0	43.5	625	2
-49	27.5	72.5	28.8	700	1
-55	22.5	77.5	18.4	875	2
-56	27.5	72.5	18.0	950	1
-58	25.5	74.5	65.0 (d)*	900	1
-60	25.0	75.0	46.3 (d)	975	2
-62	24.0	76.0	2.2	800	2
			The results at 400°C:		
B-43	90.0	10.0	2.1	800	1
-44	34.5	65.5	12.3	700	1
-50	48.5	51.5	7.6	700	1
-51	20.5	79.5	14.8	725	2
-52	13.0	87.0	5.6	725	2
-53	—	—	53.5 (d)	700	2
-54	20.5	79.5	18.0	725	2
-57	30.0	70.0	21.4	900	1
-59	26.0	74.0	64.6 (d)	1000	1
-61	21.5	78.5	41.5	925	2

* (d) indicates some decomposition.

[10] W. Walter McCarthy and J. Turkevich, J. Chem. Phys. 12 (1944), in press.

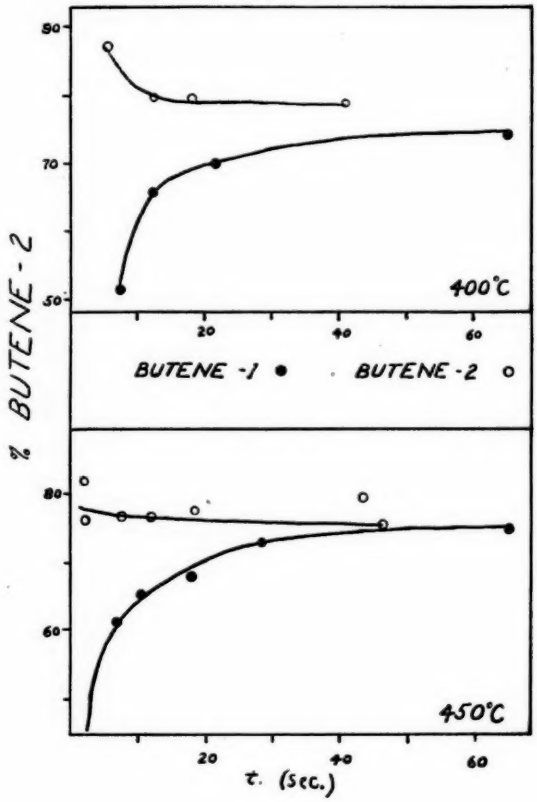

FIG. 2.

times polymerization to a low boiling liquid occurred, qualitatively more so with butene-1 than with butene-2, thus substantiating Hurd's[11] results on the relative thermal stabilities of the isomers. Upon flushing the catalyst with nitrogen after these runs the polymerization was made more evident. Smoke and vapors in very noticeable amounts were washed free of the catalyst.

DISCUSSION OF RESULTS

It is obvious that the activated alumina catalyst effected isomerization at 450°C in relatively short contact times. With butene-2 as the starting material equilibrium was attained in a few seconds. Butene-1 having a greater range to cover to reach equilibrium required in the neighborhood of 30 seconds. At such long contact times decomposition set in to a perceptible degree. At 400°C butene-2 attained equilibrium more slowly while butene-1 failed to reach the correct proportions, since the contact time necessary gave rise to acute decomposition.

The equilibrium results from this study clearly reproduce, within the accuracy of the analytical method, the figures derived from the thermodynamic data of Thacker, Folkins, and Miller.[12]

$$\Delta F_T^0 = \Delta H_0 + aT \ln T + bT^2 + cT^{-1} + I \cdot T$$

	H_0	a	b	c	I
Butene-1	9,988	32.56	−0.0188	−233,800	−153.7
Butene-2 *cis*	8,217	32.56	−0.0188	−233,800	−151.9
Butene-2 *trans*	7,267	32.56	−0.0188	−233,800	−151.3

Applying this equation ΔF_T values were calculated over the range 298.1–1200°K. The values of interest in this study are:

T°K	Butene-1	Butene-2 *cis*	Butene-2 *trans*
673	40,375	39,814	39,268
723	43,691	43,221	42,706.

Since $\Delta F_T = -RT \ln K_{eq} = -RT \ln c_1/c_2$ mole percent of butene-1 and butene-2 at equilibrium may be calculated over the range of temperature (see Fig. 3). The particular values of interest calculated from the above data are:

T°K	Butene-1	Butene-2 *cis*	Butene-2 *trans*
673	20.8	31.6	47.6
723	22.9	31.7	45.4.

These results compared with those obtained from the equilibrium study of total butene-2 mole

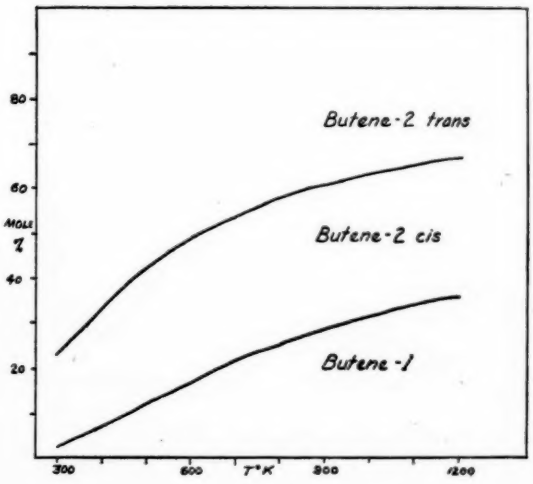

FIG. 3.

[11] C. D. Hurd and A. R. Goldsky, J. Am. Chem. Soc. **56**, 1812 (1934).

[12] Thacker, Folkins, and Miller, Ind. Eng. Chem. **33**, 584 (1941).

percent are:

	Calculated from thermodynamics	Observed
400°C	79.2	78.5±1.5
450	77.1	75.5±1.5.

It is seen that excellent agreement was obtained well within the experimental error of the analytical method.

The authors wish to express their appreciation to the M. W. Kellogg Company who financially sponsored this work, and to Professor Hugh S. Taylor for his inspiring interest.

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The Thermodynamic Properties of Gaseous Sulfur Trioxide*

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The thermodynamic properties of sulfur trioxide in the ideal gas state are calculated from molecular data. To obtain satisfactory agreement with the equilibrium data for the reaction $SO_2+\frac{1}{2}O_2=SO_3$, it is necessary to include vibrational anharmonicities, which are somewhat larger than usual because of an accidental degeneracy involving two of the normal frequencies. The standard entropy of $SO_3(g)$ at 25°C is 61.2±0.2 E.U., and its standard heat and free energy of formation from the elements are $\Delta H^\circ_{298.16}=-94.43\pm0.15$ and $\Delta F^\circ_{298.16}=-88.48\pm0.20$ kcal./mole.

INTRODUCTION

THE only accurate thermodynamic data relating to gaseous sulfur trioxide are extensive measurements[1–3] of the "contact process" equilibrium,

$$SO_3(g)=SO_2(g)+\tfrac{1}{2}O_2(g) \qquad (1)$$

in the temperature range 800°–1170°K. Since the heat capacity of sulfur trioxide has not been measured, purely thermodynamic calculations[4,5] of its standard entropy and free energy at 25° have required an arbitrary choice of ΔC_p for reaction (1), and are thus subject to considerable uncertainty.

Recently this situation has been substantially improved by Stevenson,[6] who calculated the thermodynamic properties of $SO_3(g)$ statistically from the available electron-diffraction[7] and spectral[8,9] data. The correctness of his results can be judged in the usual manner by examining the constancy of ΔH_0^0 for reaction (1) calculated from the spectroscopic values of $\Delta(F^0-H_0^0)/T$ and the experimental values of $\Delta F^0/T$. The three sets of equilibrium data lead to almost the same average values of ΔH_0^0, and the drift of the individual values with temperature was apparently judged by Yost and Russell[6] to be adequately small.

We were engaged in a similar calculation when Stevenson's work appeared. Desiring to obtain the best possible values, and believing the drift of ΔH_0^0 with temperature to be not entirely negligible, we were led to carry the investigation further. By including anharmonic contributions to the vibrational energy, we have succeeded in eliminating the trend in ΔH_0^0. Our procedure and results are described below.

THE VIBRATIONAL ASSIGNMENT

A symmetrical planar XY_3 molecule has two single and two doubly degenerate normal vibra-

* Contribution No. 511 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

[1] M. Bodenstein and W. Pohl, Zeits. f. Elektrochemie **11**, 373 (1905).

[2] G. B. Taylor and S. Lehner, Zeits. f. physik. Chemie **30** (1931).

[3] A. F. Kapustinsky and L. M. Shamovsky, Acta Physicochimica **4**, 791 (1936).

[4] G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1923), p. 551.

[5] K. K. Kelley, U. S. Bur. Mines Bull. **406**, 14 (1937).

[6] D. P. Stevenson, unpublished calculations quoted by D. M. Yost and H. Russell, Jr., *Systematic Inorganic Chemistry* (Prentice-Hall, Inc., New York, 1944), p. 314.

[7] K. J. Palmer, J. Am. Chem. Soc. **60**, 2360 (1938).

[8] H. Gerding, W. J. Nijveld, and G. J. Muller, Zeits. f. physik. Chemie **B35**, 193 (1937).

[9] H. Gerding and J. Lecomte, Physica **6**, 737 (1939).

tions.[10] From a study of the infra-red and Raman spectra of both liquid and gaseous sulfur trioxide, Gerding and Lecomte[9] chose $\nu_1(1) = 1068$ cm^{-1}, $\nu_2(2) = 1332$ cm^{-1}, $\nu_3(1) = 653$ cm^{-1}, and $\nu_4(2) = 530$ cm^{-1}, where the integers in parentheses denote degeneracies. Although the choice of ν_1 and ν_2 is unequivocal, this assignment is open to several objections: A moderately strong and sharp band at 1123 cm^{-1} in the vapor infra-red spectrum is left unexplained, while the extreme broadness of the absorption around 650 cm^{-1} renders the value assigned to ν_3 very uncertain. It should also be pointed out that the band at 530 cm^{-1} was observed only in the Raman spectrum of the *liquid* (known to be extensively polymerized); thus, while its augmented intensity with increased temperature or dilution (in liquid sulfur dioxide) identifies it as a monomer absorption, the numerical value may be somewhat altered.

Stevenson[6] made a more attractive assignment by ignoring the doubtful band at 653 cm^{-1}, setting $\nu_3 = 530$ cm^{-1}, and attributing the 1123 cm^{-1} infra-red band to the overtone $2\nu_4$ (in agreement with selection rules), thus placing ν_4 at about 560 cm^{-1}.

When the thermodynamic properties are calculated with each of these assignments, there is little to choose between them. With the original assignment of Gerding and Lecomte, the standard entropy of $SO_3(g)$ at 298.16°K is calculated to be 61.09 E. U., and ΔH_0^0 for reaction (1) has the average value 23.03 kcal. For the Bodenstein-Pohl data,[1] which span the widest temperature range and appear to be the most consistent, the individual ΔH_0^0 values show a drift of 0.40 kcal. over a 370° interval. With his alternative assignment, Stevenson[6] found $S^\circ_{298.16} = 61.19$ E. U., an average ΔH_0^0 of 22.97 kcal., and a drift of 0.35 kcal.

There are two possible ways of eliminating the trend in ΔH_0^0. One is to brand the spectral data as inadequate and adjust one of the lower frequencies ν_3 or ν_4 until the trend is eliminated; this device has frequently been employed to assign frequencies that have not been observed. In this way, it is found that one of the low frequencies must be taken at about 400 cm^{-1}. This result is untenable when viewed in the light of several approximate calculations. Either by employing a simple valence-force potential with the force-constants equal to those for SO_2 (justified by the similarity of bond distances and angles), or by taking the general potential function[10] with force-constants about the same as those for the electronically similar carbonate and nitrate ions, one finds a lower limit of about 500 cm^{-1} for both ν_3 and ν_4. Thus the general distribution of frequencies in either of the assignments discussed above cannot be far from correct.

The other method, which we have followed, is to supplement one of the given assignments by the inclusion of anharmonic terms. For most molecules, these terms would be too small to play the role we require of them, but for SO_3 our procedure is readily justified. It will be noted that the frequency 530 cm^{-1} (which is retained as either ν_3 or ν_4 in the alternative assignments) happens to be almost exactly half of $\nu_1 = 1068$ cm^{-1}. That such an accidental degeneracy can cause considerable perturbation of the vibrational levels was first pointed out by Fermi[11] in discussing the spectrum of CO_2, and an examination of the cubic terms in the potential energy[10] shows that this effect should actually exist in SO_3, irrespective of whether the 530 cm^{-1} frequency is taken as ν_3 or ν_4. The 1123 cm^{-1} infra-red band could thus be either $2\nu_3$ or $2\nu_4$. More important for the purpose at hand, it is therefore justifiable to assign abnormally large values to certain of the anharmonic terms in the vibrational energy, if necessary. As will be shown in the next section, the values required are by no means excessive.

CALCULATIONS AND RESULTS

The S–O distance in the planar symmetrical SO_3 molecule (symmetry number 6) is[7] 1.43 ±0.02A. Accordingly, the free energy of the ideal gas at atmospheric pressure is found[12] to be

$$-(F^0 - H_0^0)/RT = 3.126 + 4 \ln T + \ln Q_v, \quad (2)$$

[10] For a representation of the normal modes, see (for example) S. Silver and W. H. Shaffer, J. Chem. Phys. **9**, 599 (1941).

[11] E. Fermi, Zeits. f. Physik **71**, 250 (1939).

[12] We have used the formulae given by J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), pp. 440–454, which are based on universal constants slightly different from those of the I.C.T. Compared to other uncertainties in the calculation, the difference is inconsequential.

where Q_v is the vibrational partition function. The contributions of nuclear spin and isotope mixing are omitted, as is customary, and a single non-degenerate electronic level is assumed.

The vibrational energy of a polyatomic molecule will be taken as

$$E_v/hc=\sum \omega_i(v_i+d_i/2) -\sum_{i\leq j} X_{ij}(v_i+d_i/2)(v_j+d_j/2), \quad (3)$$

where v_i, d_i are quantum numbers and degeneracies, respectively. In this expression, the anharmonic terms involving the azimuthal quantum numbers of the degenerate vibrations have been omitted for simplicity, but it can be shown that their contributions to the thermodynamic functions are of the same general form as those of the terms which have been retained. The quantities

TABLE I. Molecular constants of SO_3.

S−O distance = 1.43±0.02A
O−S−O angle = 120°
Principal moments of inertia:
$I_A=I_B=\frac{1}{2}I_C=(8.15\pm0.2)\times10^{-39}$ g cm²
Symmetry number = 6
Fundamental frequencies (cm^{-1})

$\nu_1(1)=1068$	$\nu_3(1)=530$
$\nu_2(2)=1332$	$\nu_4(2)=560$

Vibrational anharmonicities (cm^{-1})

$X_{11}=6.4$	$X_{14}=4.9$	$X_{33}=42.4$
$X_{12}=7.2$	$X_{22}=8.0$	$X_{34}=3.3$
$X_{13}=63.9$	$X_{23}=5.6$	$X_{44}=3.4$
	$X_{24}=5.7$	

ω_i are the purely harmonic normal frequencies, which are not identical with the observed fundamentals ν_i. The latter are given by

$$\nu_k=\omega_k-X_{kk}(1+d_k) -\sum_{i<k} X_{ik}d_i/2-\sum_{k<j} X_{kj}d_j/2. \quad (4)$$

By substituting this expression into Eq. (3) and subtracting the zero-point energy, the vibrational levels can be written

$$(E_v-E_0)/hc=\sum \nu_i v_i-\sum X_{ii}v_i(v_i-1) -\sum_{i<j} X_{ij}v_iv_j. \quad (5)$$

Each value of a quantum number v_i corresponds to $\binom{v_i+d_i-1}{v_i}$ states. If the anharmonic terms in Eq. (5) are considered small, so that their contribution to the Boltzmann factor can be expanded, the vibrational partition function can readily be summed, and is found[13] to be

$$Q_v=\prod_i[1-\exp(-u_i)]^{-d_i}[1+\sum_{i\leq j} f_{ij}+\cdots], \quad (6)$$

where

$$u_i=hc\nu_i/kT, \quad (\nu_i \text{ in } cm^{-1}),$$

$$f_{ii}=d_i(d_i+1)X_{ii}hc/kT[\exp(u_i)-1]^2$$

and

$$f_{ij}(i<j)=d_id_jX_{ij}hc/kT \times[\exp(u_i)-1][\exp(u_j)-1].$$

It is apparent that the last factor in Eq. (6) is a correction to the result which would have been obtained by assuming harmonic oscillators with frequencies ν_i. The additive free-energy correction per mole is thus given by

$$-F_c/RT\leqq\ln(1+\sum_{i\leq j} f_{ij})\leqq\sum_{i\leq j} f_{ij}. \quad (7)$$

At sufficiently high temperatures, f_{ij} becomes practically a linear function of T, as can be seen by expansion of the expressions given under Eq. (6). In the temperature range of the equilibrium data, this will be true for those terms involving the low frequencies ν_3 and ν_4. At room temperature, on the other hand, every f_{ij} is almost negligible. Accordingly, Stevenson's value of the standard entropy at 25°C will scarcely be changed by this refinement, but ΔH_0^0 will be noticeably affected. If only these quantities were desired, it would probably be legitimate, in view of the virtual *carte blanche* furnished by the accidental degeneracy, to choose for $-F_c/RT$ an empirical linear function of T such that the drift in ΔH_0^0 is eliminated. However, since we wished also to compute the thermodynamic properties at intermediate temperatures, a more definite procedure was followed, as described below.

The frequency assignment of Stevenson

$$(\nu_3=530,\ \nu_4=560)$$

was used in our final calculations; from the previous discussion it is evident that the Gerding-Lecomte assignment would yield almost identical results. Then the only anharmonic terms in Eq. (5) to be affected by the accidental degeneracy

[13] Compare the method used for diatomic molecules by Mayer and Mayer, reference 12, pp. 160–166, or that of L. S. Kassel, J. Am. Chem. Soc. **56**, 1838 (1934).

TABLE II. ΔH_0^0 for the reaction $SO_3(g)=SO_2(g)+\frac{1}{2}O_2(g)$.

Ref.	T(°K)	$(\Delta F^0/T)_{obs.}$	ΔH_0^0(kcal.)
1	801	6.84	22.66
	852	5.21	22.73
	900	3.73	22.69
	953	2.33	22.70
	1000	1.23	22.72
	1062	−0.09	22.72
	1105	−0.93	22.70
	1170	−2.05	22.70
			Av. 22.70±0.02
2	933	2.88	22.74
	936	2.75	22.69
	943	2.53	22.65
	945	2.48	22.65
	945	2.53	22.70
			Av. 22.69±0.03
3	850	5.10	22.58
	852	4.96	22.52
	876	4.59	22.83
	876	4.45	22.71
	902	3.74	22.75
	919	3.03	22.53
	941	2.72	22.78
	954	2.41	22.80
	965	1.95	22.62
	1001	1.24	22.75
	1001	1.28	22.79
			Av. 22.70±0.10
	Grand average, $\Delta H_0^0=22.70\pm0.10$ kcal.		

are those[14] in X_{13} and X_{33}. All the others will presumably have normal values, whose magnitudes can be estimated. For example, Redlich[15] has shown that X_{ii} for a stretching vibration in a polyatomic molecule is very nearly the same as that for a diatomic molecule of the same normal frequency and bond energy. Furthermore, all the various X_{ij} in a given molecule are roughly proportional (in the absence of a "Fermi resonance") to the frequencies involved. Thus, using the diatomic molecule SO as a guide,[16] we have set

$$X_{ij}=0.003(\nu_i+\nu_j) \text{ (except } X_{13} \text{ and } X_{33}), \quad (8)$$

and have also used this equation to evaluate anharmonic corrections for SO_2. Postulating an equation of the same form (but with a larger numerical factor) to govern X_{13} and X_{33}, we are left with but one numerical constant to be determined by the requirement that ΔH_0^0 shall not drift. By trial and error, it was found that the equation

$$X_{ij}=0.040(\nu_i+\nu_j), \quad (X_{13} \text{ and } X_{33} \text{ only}) \quad (9)$$

leads to acceptable results. It is satisfying that these anharmonicities are only about ten times "normal" values. A summary of the molecular constants adopted for our final calculations is given in Table I.

The final determination of ΔH_0^0 for reaction (1) is summarized in Table II. It is apparent that no trend remains, and this was verified by least-squaring a linear equation through the points. In obtaining these results, the published spectroscopic values of $(F^0-H_0^0)/T$ for oxygen[17] and sulfur dioxide[18] were used. The former already contain anharmonic corrections, and the latter were amended, as described above, with the aid of Eqs. (6)–(8), although this produced practically no change in the results. It is a coincidence that the average values of ΔH_0^0 for the three sets of data are in almost perfect agreement.

To check the value of ΔH_0^0, we also made calculations with the Gerding-Lecomte assignment. In this case a slightly larger anharmonic correction is needed, but because ν_4 is doubly degenerate the required values of X_{14} and X_{44} are not so large, the numerical factor in the analog of Eq. (9) being only 0.022. This calculation leads to an average ΔH_0^0 identical with that given in Table II. It therefore appears safe to set $\Delta H_0^0=22.70\pm0.10$ kcal. for reaction (1). Our calculations for this reaction at 25°C are

TABLE III. Thermodynamic data for the reaction $SO_3(g)=SO_2(g)+\frac{1}{2}O_2(g)$ at 25°C.

Source	$\Delta F^\circ_{298.16}$(kcal.)	$\Delta S^\circ_{298.16}$(E. U.)	$\Delta H^\circ_{298.16}$(kcal.)
Lewis and Randall[a]	16.23	21.36	22.60
Kelley[b]	15.90	20.15	21.90
Stevenson[c]	16.96	——	——
Bichowsky and Rossini[d]	——	——	23.0
This paper	16.77	22.53	23.49

[a] See reference 4. [b] See reference 5. [c] See reference 6. [d] See reference 19.

[14] See Silver and Shaffer, reference 10, Eq. (22a).
[15] O. Redlich, J. Chem. Phys. **9**, 298 (1941).
[16] Mayer and Mayer, reference 12, p. 469.
[17] H. L. Johnston and M. K. Walker, J. Am. Chem. Soc. **55**, 172 (1933).
[18] P. C. Cross, J. Chem. Phys. **3**, 825 (1935), as corrected by W. F. Giauque and C. C. Stephenson, J. Am. Chem. Soc. **60**, 1389 (1938).

TABLE IV. Thermodynamic functions of sulfur trioxide (hypothetical ideal gas at 1 atmos. pressure).

T(°K)	$-(F^0-H_0^0)/T$ cal./deg./mole	S^0 cal./deg./mole	$(H^0-H_0^0)$ kcal./mole	C_p^0 cal./deg./mole
298.16	51.94	61.24	2.77	12.10
300	52.00	61.32	2.80	12.13
400	54.81	65.07	4.10	14.05
500	57.17	68.36	5.60	15.66
600	59.31	71.35	7.22	16.89
700	61.23	74.03	8.96	17.85
800	62.98	76.46	10.78	18.61
900	64.61	78.69	12.67	19.22
1000	66.12	80.75	14.63	19.75
1100	67.54	82.65	16.63	20.20
1200	68.87	84.42	18.67	20.59

TABLE V. Contributions of vibrational anharmonicity to thermodynamic functions of $SO_3(g)$.

T(°K)	$-F_e$ (cal./mole)	H_e (cal./mole)	S_e (cal./deg./mole)	C_e (cal./deg./mole)
300	2.4	18	0.07	0.16
600	56	153	0.35	0.79
1000	310	628	0.94	1.56

compared with those of previous investigators in Table III.

By combination of our results for reaction (1) with the accurate thermochemical heat of formation of sulfur dioxide[19] and the accurate entropy values for sulfur[20] and oxygen,[17] the following constants for the formation of sulfur trioxide from the elements are obtained:

$$S(rh)+\tfrac{3}{2}O_2(g)=SO_3(g); \qquad (10)$$

$$\Delta F^\circ_{298.16}=-88.48\pm0.20 \text{ kcal.};$$

$$\Delta H^\circ_{298.16}=-94.43\pm0.15 \text{ kcal.};$$

$$\Delta S^\circ_{298.16}=-19.95\pm0.20 \text{ E. U.}$$

These figures are more trustworthy than those tabulated by Yost and Russell,[6] who give the early free-energy value of Lewis and Randall[4] and the rather uncertain thermochemical[19] heat of formation.

The calculated thermodynamic properties of sulfur trioxide in the ideal gas state are presented in Table IV, for the temperature range 298°–1200°K. The magnitudes of the anharmonic contributions to these figures can be judged from the several representative values given in Table V. The standard entropy of $SO_3(g)$ can be taken as $S^\circ_{298.16}=61.2\pm0.2$ E. U.

It is a pleasure to acknowledge helpful discussions with Drs. C. C. Stephenson and L. Tisza.

[19] F. R. Bichowsky and F. D. Rossini, *Thermochemistry of the Chemical Substances* (Reinhold Publishing Corporation, New York, 1936), pp. 27–28.

[20] E. D. Eastman and W. C. McGavock, J. Am, Chem. Soc. **59**, 145 (1937).

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Effect of Deformation on the Swelling Capacity of Rubber

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Elongation of swollen vulcanized rubber, or other polymeric materials possessing random network structures, should increase the amount of liquid absorbed (dissolved) at equilibrium with an excess of the swelling agent. According to a previously published equation relating to the thermodynamics of stretching and swelling of rubber, the relative volume of the swollen rubber at equilibrium should equal the square root of the relative stretched length. Experiments with butyl rubber vulcanizates in xylene support these predictions of theory.

IN a recent paper[1] dealing with the thermodynamics of swelling of vulcanized rubber in solvents, the following equation was derived to express the entropy change in passing from the *unstressed, unswollen* state to the *stretched, swollen* state,

$$\Delta S_{d,s}=-kn\ln[n/(n+Zv)] -(3/2)kv\left[\left(\frac{n+Zv}{Zv}\right)^{\frac{2}{3}}(\alpha^2+2/\alpha)/3-1\right], \qquad (1)$$

[1] P. J. Flory and J. Rehner, Jr., J. Chem. Phys. **11**, 521 (1943).

where k is Boltzmann's constant, n is the number of solvent molecules, ν is the number of "chains" or portions of rubber molecules between cross linkages of the vulcanizate network, Z is the ratio of the volume of a chain to the volume of a solvent molecule, and α is the ratio of the length of the *elongated, swollen* sample to its length in the *unstressed, swollen* condition. From this equation the effects of swelling on elastic properties and the influence of stretching on swelling capacity can be predicted.

In our previous paper[1] we drew the incorrect conclusion from the above equation that the rubber gel, in equilibrium with excess solvent, should de-swell when stretched. In obtaining this result, Eq. (1) was differentiated with respect to n to obtain a partial molal entropy at constant α, instead of at constant absolute length. The equilibrium condition so introduced applies only to the rather artificial situation in which the rubber is stretched such that its length is always α times the length it would assume at the same degree of swelling in the absence of stress (recalling the definition of α). In other words, the length L of sample is to be adjusted in conformity with

$$L=\alpha L_0 V^{\frac{1}{3}},$$

where L_0 is the unstressed, unswollen length and V is the volume swelling ratio (volume of gel/volume of dry rubber), and α is fixed. It is the purpose of this note to show, contrary to a statement which occurs in our preceding paper,[2] that Eq. (1) predicts an *increase* in equilibrium swelling volume with increase in the absolute length to which the swollen sample is stretched. Experimental results are included below in support of this deduction.

Introducing a new stretch factor α' defined as the ratio of the *stretched, swollen* length to the *unstretched, unswollen* length

$$\alpha'=L/L_0=\alpha V^{\frac{1}{3}},$$

where the volume swelling ratio V is given alternatively by

$$V\equiv(n+Z\nu)/Z\nu\equiv 1/v_2,$$

where v_2 is the volume fraction of rubber in the swollen gel. Substituting

$$\alpha=\alpha'[Z\nu/(n+Z\nu)]^{\frac{1}{3}}$$

in Eq. (1) and differentiating with respect to n at constant α', there is obtained for the partial molal free energy of solvent

$$\Delta\bar{F}_1(\text{const. }\alpha')$$
$$=RT[\ln(1-v_2)+v_2+Kv_2^2/2+1/\alpha' Z], \quad (2)$$

the third term of which represents a van Laar heat of mixing term.[3] For equilibrium with excess solvent to prevail at constant length, $\Delta\bar{F}_1$ (const. α') must equal zero. At equilibrium, therefore,

$$-[\ln(1-v_2)+v_2+Kv_2^2/2)]=1/\alpha' Z. \quad (3)$$

Taking v_2 to be small (large swelling), expansion of the logarithmic term in series yields the approximate expression

$$1/V=v_2\cong[2/\alpha' Z(1-K)]^{\frac{1}{2}}. \quad (3')$$

In the unstretched, swollen sample $\alpha'=V^{\frac{1}{3}}$. Hence, writing V_0 for the swelling volume in the unstretched, swollen condition

$$V/V_0=(\alpha'/V_0^{\frac{1}{3}})^{\frac{1}{2}}=(\alpha'/\alpha_0')^{\frac{1}{2}}. \quad (4)$$

Thus, the swelling volume is predicted to increase in proportion to the square root of the length. These same equations may be applied to simple compression, where $\alpha'<\alpha_0'$.

Experimental measurements on the influence of stretching on swelling were conducted on molded rings of pure gum butyl rubber, 0.25 in. wide by about 0.050 in. thick and having a mean diameter of 1.00 in. These were prepared by curing a compound consisting of 100 parts B-1.5 butyl rubber, 1.0 part zinc oxide, 1.5 parts sulfur, and 1.0 part tetramethylthiuram disulfide for one hour at 153°C. The swelling liquid was reagent-grade xylene containing 0.05 percent phenyl β-naphthylamine antioxidant.

A ring was weighed to the nearest mg, and two $\frac{5}{16}$-in. glass rods of short length were inserted through it. One of these served as an upper (fixed) support; to the other a lead weight

[2] Second line, p. 526 of reference 1.

[3] In analogous equations of previous papers we have replaced Z with $M_c/\rho V_1$ where M_c is the molecular weight per chain of relative volume Z, ρ is the density of the dry rubber, and V_1 is the molar volume of the solvent.

was attached. The assembly consisting of glass rods, rubber ring, and weight, was immersed in the xylene contained in a tall cylinder. This procedure was adopted after it had been found that stretching to an arbitrary field length followed by immersion in solvent invariably resulted in rupture. A considerable tension is required to achieve the desired elongation prior to swelling. In the presence of solvent the strength is so much reduced that rupture occurs before the tension can be sufficiently relieved by swelling. In the method adopted here elongation proceeds concurrently with swelling, and at no time is the rubber subjected to a high stress.

After allowing swelling to proceed at room temperature in darkness for 24 hours, the over-all vertical length of the loop was measured with a cathetometer. From this length, the diameters of the glass rods, and the approximate thickness of the swollen rubber, the mean circumferential length of the swollen specimen was computed (fourth column of Table I). The assembly was then removed from the xylene bath, excess solvent was blotted away with filter paper while the sample remained under tension, and the sample was immediately removed and placed in a weighing bottle and weighed. Thereafter the ring was again installed between the glass rods and replaced in the xylene under tension as before. Measurements were repeated after additional periods of 24 and 96 hours. Weights of the swollen rings for one, two, and five days immersion agreed within the experimental error—about ± 0.01 gram. Average weights are recorded in the third column of Table I.

Taking 0.93 and 0.86 for the densities of the butyl compound and the xylene, respectively, the volumes of dry rubber and swollen gel were computed. (The volume change on mixing is negligible.) Their ratio, the swelling ratio V, is given in the fifth column. The relative lengths α' were computed by dividing the absolute lengths of the fourth column by 7.98 cm, the mean circumferential length of the unstretched, unswollen ring.

The observed ratio of the V's for stretched and unstretched samples are given in the next to the last column. Values calculated from α' and α_0' using Eq. (4) are given in the last column. Comparisons between these two columns show that the observed effect of elongation on swelling is in the proper direction and that its magnitude approximates the predictions of theory.

TABLE I. Effect of elongation on equilibrium swelling.

Load in g*	Weight of butyl ring, g	Weight of swollen ring, g	Mean circumferential length of swollen ring, cm	Swelling ratio V	α'	V/V_0 Obs.	V/V_0 Calc.
0	0.570	3.06	(14.20)**	5.72	(1.78)**		
50	0.570	3.11	15.45	5.81	1.93	1.01_6	1.04
100	0.564	3.13	16.41	5.92	2.06	1.03_5	1.07_5
150	0.568	3.44	18.15	6.46	2.27	1.13	1.13

* Uncorrected for buoyancy of xylene on submerged weight.
** Values calculated from swelling ratio; i.e., α' for zero load equals $V^{\frac{1}{3}}$, since swelling is isotropic.

The set of results shown in the table was obtained on four different rings. Some of the irregularity undoubtedly is owing to variations in cure from one ring to another, although all of these were cured from the same compound under as nearly identical conditions as possible. The increase in swelling with elongation is reversible. In an experiment to check this point, removal of the load from the ring was followed by a decrease in swelling volume to the same value obtained on another unstressed sample of the same rubber.

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The Kinetics of the Electroreduction of Acetone*

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The electrolytic reduction of acetone in alkaline aqueous solutions at a mercury surface has been studied with the object of determining the kinetics of the formation of isopropyl alcohol and pinacol. The reduction rate has been studied at various acetone concentrations, in varying concentrations of sodium hydroxide, in solutions of sodium sulfate, sodium chloride, barium hydroxide, and potassium hydroxide. During electrolysis the rates of formation of isopropyl alcohol and pinacol were followed continuously. It is found that at low acetone concentrations the rate of formation of isopropyl alcohol is proportional to the acetone concentration, while the rate of formation of pinacol is proportional to the square of the acetone concentration. At somewhat higher acetone concentrations the pinacol rate becomes linear in acetone concentration, and near saturation the isopropyl alcohol rate becomes practically independent of acetone concentration. At constant current density, increasing the sodium hydroxide concentration decreases the yield of isopropyl alcohol and increases the yield of pinacol (except at high concentrations of acetone and sodium hydroxide). Substitution of chloride or sulfate for hydroxide causes an increase in the alcohol rate but lowers the pinacol rate. Substitution of barium for sodium stops the reduction completely. Substitution of potassium for sodium increases both yields. Increasing the current density is accompanied by a decrease in the fraction of the current which goes into isopropyl alcohol formation and pinacol formation. It is shown that these experimental results can be explained by a modification of the mechanism proposed by Müller. The acetone is first adsorbed on the mercury with the formation of a covalent bond. The product of the adsorption may dissociate from the surface as a free radical, in which case pinacol is the final product, or it may first add on a proton and then dissociate from the surface as an ion which adds a second proton to become isopropyl alcohol.

INTRODUCTION

THE reduction of acetone by an electric current presents a number of problems of which the most important are the effect of conditions on the current efficiency of the reduction, and the effect of conditions on the stage at which the reduction stops. Acetone, like all uncharged molecules, can be reduced only in the presence of an electrolyte. Under nearly all conditions this electrolyte is also reduced at the cathode.

The reduction in acid solutions has been studied by Tafel,[1] by Schall,[2] and by Müller.[3] In these solutions hydrogen is formed by the reduction of hydrogen ions, and it has been proposed by Leslie and Butler[4] that the reduction of acetone is caused by a secondary reaction of hydrogen atoms produced at the cathode. In these solutions the reduction products are isopropyl alcohol, propane, and mercury di-isopropyl if a mercury cathode is used.

The reduction in alkaline solutions has been studied by Wilson and Wilson.[5] In these solutions, with mercury cathodes, hydrogen is not formed. If sodium or potassium hydroxide is used as the electrolyte, alkali ions are reduced, forming sodium or potassium amalgam. Under these conditions atomic hydrogen would not be expected to be the reducing agent, and it seems more plausible that the acetone is directly reduced at the mercury surface. In these solutions the acetone is reduced only to isopropyl alcohol and pinacol.

Müller[3] has proposed the following mechanism: The base step in the reduction is the formation of a covalent bond between the central carbon atom of the acetone molecule and the cathode surface. The resulting surface compound has the structure

$$\begin{array}{c} \mathrm{OH} \\ | \\ \mathrm{CH_3-C-CH_3}, \\ | \\ [M] \end{array}$$

the $[M]$ being a metal atom in the cathode surface. Müller postulates that this is formed by the hydration of acetone, followed by a displacement of one of the two resulting hydroxyls by the

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

[1] J. Tafel, Zeits. f. Elektrochemie **17**, 972 (1911).
[2] C. Schall, Zeits. f. Elektrochemie **29**, 537 (1923).
[3] E. Müller, Zeits. f. Elektrochemie **33**, 253 (1927).
[4] W. M. Leslie and J. A. V. Butler, Trans. Faraday Soc. **32**, 989 (1936).
[5] C. L. Wilson and K. B. Wilson, Trans. Electrochem. Soc. **80**, 151 (1941).

metal atom:

$$CH_3C(OH)_2CH_3+M+e \rightarrow CH_3COHMCH_3+OH^-. \quad (1)$$

If this surface compound now ionizes, the result is an ion

$$\left(\begin{array}{c} OH \\ | \\ CH_3—C—CH_3 \\ \cdot\cdot \end{array}\right)^-,$$

the reaction involving a second reduction:

$$CH_3COHMCH_3+e \rightarrow [CH_3COHCH_3]^-+[M]. \quad (2)$$

This ion may now pick up a proton to form isopropyl alcohol

$$[CH_3COHCH_3]^-+H^+ \rightarrow CH_3CHOHCH_3. \quad (3)$$

Alternatively the ion may react with an acetone molecule to form a pinacolate ion

$$\left(\begin{array}{c} OH \\ | \\ CH_3—C—CH_3 \\ \cdot\cdot \end{array}\right)^- + CH_3COCH_3$$

$$\rightarrow \left(\begin{array}{c} OH \\ | \\ CH_3—C—CH_3 \\ | \\ CH_3—C—CH_3 \\ | \\ O \end{array}\right)^-, \quad (4)$$

which picks up a proton to give pinacol. Müller also extends this mechanism to explain the formation of propane.

This work was undertaken to examine the kinetics of this reduction more closely, and to determine the effect of changing electrolyte and current density on the yields of the various products. As it will presently appear, the results do not agree entirely with Müller's mechanism, but a few slight changes in the mechanism produce agreement.

EXPERIMENTAL METHODS

Two different electrolytic cells were used. For concentrated solutions the cell was of approximately 200 milliliters capacity. The anode was a platinum wire bent around a cooling tube. The anode compartment was separated from the cathode compartment by a porous porcelain cup. A stirrer agitated both the catholyte and the mercury cathode. For further stirring to remove sodium amalgam from the mercury surface, the mercury was forced by a siphon and suction arrangement to rise and fall in a side tube which contained strong acid. About one-fifth of the mercury was forced into the side tube every ten seconds. A side arm was provided for withdrawing samples and passing gases through the solution. The cell was closed by rubber stoppers which had been previously boiled in vacuum with paraffin.

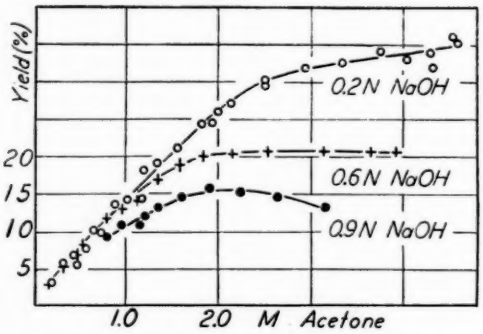


FIG. 1. Yield of alcohol plotted against molarity of acetone. Current density 0.0637 amp./cm².

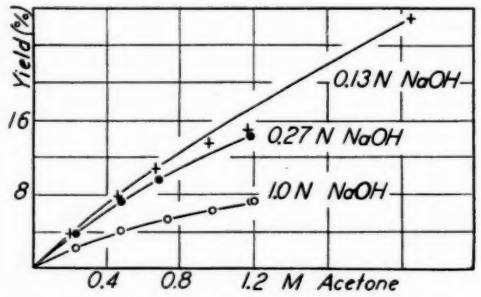


FIG. 1a. Yield of alcohol plotted against molarity of acetone. Current density 0.0360 amp./cm².

For dilute solutions a smaller cell of approximately 65-ml capacity was used. This was of generally similar construction to the larger, but it was not provided with a side arm for passing in gases. The dilute solutions also required more violent agitation of the mercury in order to keep the amalgam concentration low enough to obtain reproducible results. The siphon which regulated the suction in the deamalgamation side tube was therefore modified so that half of the mercury in the cell was drawn into the side arm every ten seconds.

Runs were made in series in the following way.

The cathode compartment was first filled with a solution of the desired composition, and the anode compartment with 10 *N* sodium hydroxide. The electrolysis was then begun, adjusting the potential to keep a constant current density (usually 0.0637 amp./cm²—a total current of 0.800 amp.). The run was always stopped before there was a large change in the composition of the solution. At this point a sample of the cathode was withdrawn for analysis, but the current was kept flowing in order to prevent any sodium amalgam present from reacting with the solution. Fresh solution was added immediately in such amounts as would produce approximately the desired composition for the next run, and the next run was begun immediately. The exact composition for the new run was calculated later from the analysis of the solution at the end of the previous run and the amounts of material added. For each run the average of the compositions of the catholyte at the beginning and end was used in plotting the results.

It was found that diffusion of the reaction products (isopropyl alcohol and pinacol) through the porous cup was negligible. Nevertheless the variation in results noted by Wilson and Wilson[5] on changing porous cups was confirmed. The effect, although small, was outside the limits of experimental error, and no other explanation can be offered than that suggested by them on the basis of irregularities in the distribution of the current over the cathode surface caused by irregularities in the porous cup. Most of the results reported here were obtained with two cups which gave consistent results.

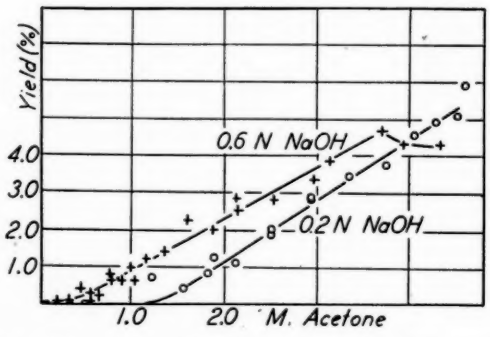


FIG. 2. Yield of pinacol plotted against molarity of acetone. Current density 0.0637 amp./cm².

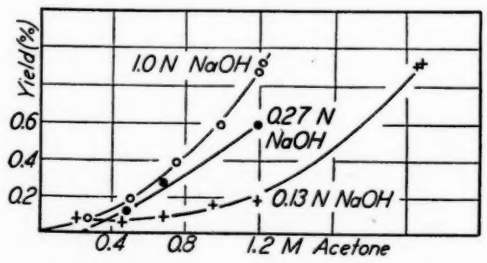


FIG. 2a. Yield of pinacol plotted against molarity of acetone. Current density 0.0360 amp./cm².

In a number of blank electrolyses it was found that neither isopropyl alcohol nor pinacol was reduced under the conditions used in these experiments.

The samples taken were diluted to 50 ml, if necessary, with dilute sulfuric acid so that the alkali concentration did not exceed 0.2 normal. They were analyzed by the following procedures.

Acetone was analyzed by converting it to iodoform and titrating the excess iodine. The precautions necessary in this procedure have been summarized by Goodwin.[6] We had ample opportunity to confirm the justification of all the precautions listed by Goodwin. Isopropyl alcohol and pinacol were never concentrated enough to interfere in this analysis.

Total alcohol and pinacol were determined by oxidation with standard dichromate.[7] A 10-ml sample approximately 0.01 *M* in alcohol in a dry flask was mixed with an equal volume of ice-cooled 0.1 *N* acidified standard dichromate, containing 18 *N* sulfuric acid. The mixture was kept in a thermostat at 25° for one hour, and was then diluted with 200 ml of ice-cold water, mixed with a potassium iodide solution, and titrated with sodium thiosulfate. It was found essential to precool the standard dichromate to prevent overheating during mixing, and also to perform the titration in an ice-cold solution to slow down the reaction between acetone and iodine which otherwise leads to fading end points. The results were reproducible to better than one percent, but a correction factor had to be introduced since the oxidation was not complete in one hour. This factor was determined by oxidations on known solutions to be 1.057.

Acetone was slightly oxidized by this procedure so that further corrections had to be

[6] L. F. Goodwin, J. Am. Chem. Soc. 42, 39 (1920).
[7] H. A. Cassar, Ind. Eng. Chem. 19, 1061 (1927).

made. The oxidation of acetone was apparently owing to the presence of diacetone alcohol formed in alkaline acetone solutions. This oxidation correction for acetone was determined for a series of solutions varying in acetone, alkali, and salt concentration. The correction factor increased linearly with the acetone concentration. In a 0.1 *M* acetone solution, 4.85×10^{-4} mole per liter of acetone, or 0.5 percent, was oxidized. For a given acetone concentration the oxidation factors remained independent of the alkali concentration up to at least 0.2 *N*, but the factor increased if the alkali concentration exceeded this value considerably. However, even a strongly alkaline solution of excessively large oxidation factor was found to return to a normal oxidation factor within a few hours after the excess alkali had been neutralized. The salt concentration did not affect the oxidation. For these reasons analyses on solutions which had at some time contained large concentrations of alkali were performed at least 24 hours after the sample had been diluted or neutralized. Acid solutions did not give a constant correction factor and were avoided.

Pinacol was determined by oxidation with periodic acid.[8] Isopropyl alcohol did not interfere. A very small amount of acetone was oxidized by periodic acid, amounting to 0.030 percent of the acetone concentration. It was confirmed that this correction does not depend on alkali or salt concentration.

Sulfate ion was determined by adding an excess of standard barium chloride after neutralization, and titrating with standard sodium carbonate solution using phenolphthalein.

Chloride ion was determined by the method of Mohr.[9] *Materials* acetone was redistilled twice, the first time from alkaline permanganate. It boiled at 56°.

Distilled water was freshly boiled to remove dissolved air.

Sodium hydroxide was rendered carbonate free by preparing a saturated solution.

Standard solutions of isopropyl alcohol were prepared from alcohol which had been dried over calcium oxide, redistilled over magnesium and a trace of iodine, and boiled at 60°.

The pinacol for standard solutions was recrystallized twice from water, dried first on a porous plate, then on filter paper, and weighed out immediately.

[8] N. Allen, H. Y. Charbonnier, and R. M. Coleman, Ind. Eng. Chem. Anal. Ed. 12, 384 (1940).

[9] H. H. Willard and N. H. Furman, *Elementary Quantitative Analysis* (D. Van Nostrand Company, Inc., New York, 1939).

RESULTS

In order to put all of the experimental results on the same basis, the yield of isopropyl alcohol in moles for each run has been multiplied by 200 and divided by the number of faradays of current passed, and the yield of pinacol has been treated in the same way. Since the formation of a mole of either isopropyl alcohol or pinacol requires the use of two faradays, the numbers so obtained represent the percent of the current passed, which was used in the production of isopropyl alcohol or pinacol. Because of transport of metallic ions through the porous cup, it was not possible to measure exactly the amount of metallic ions reduced, but approximate measurements showed that the reduction of metallic ions was of the right order of magnitude to account for the balance of the current. Since there was no evidence of any other reduction process, the amount of reduction of metallic ions has been obtained by difference.

All measurements were made at 25°±0.03°.

The first series of measurements were made to show the effect of acetone concentration on the yields of isopropyl alcohol and pinacol. These runs were made at a current density of 0.0637 amp./cm², and in 0.2 *N*, 0.6 *N*, and 0.9 *N* NaOH. The results are shown in Figs. 1 and 2. A second similar series of runs was made at a lower current density of 0.0360 amp./cm² for the more dilute acetone solutions, using 0.13 *N*, 0.27 *N*, and 1.0 *N* NaOH as the electrolyte. These results are shown in Figs. 1a and 2a.

These figures show immediately that the yield of isopropyl alcohol in dilute acetone solutions is proportional to the acetone concentration. The yield of pinacol, on the other hand, at the lowest concentrations is proportional to the square of the acetone concentration. At moderate concentrations the pinacol yield is linear in the acetone concentration. Finally, at the highest concentrations of acetone, approaching saturation, the isopropyl alcohol yield reaches a limiting value

which depends strongly on the alkali concentration.

The same figures show that increasing the alkali concentration lowers the yield of isopropyl alcohol and increases the yield of pinacol, but in such a way that there is a net decrease in the amount of the acetone reduced. To study this effect further, a series of runs was made, again at a current density of 0.0637 amp./cm², but this time varying the NaOH concentration while the acetone concentration was held constant at 3.7 *M*, 3.0 *M*, 1.7 *M*, and 1.4 *M*. The results are shown in Fig. 3. It should be noted that in this figure the reciprocal of the isopropyl alcohol yield is plotted against the NaOH concentration. Theoretical considerations to be given later suggest that this plot should give a straight line. It

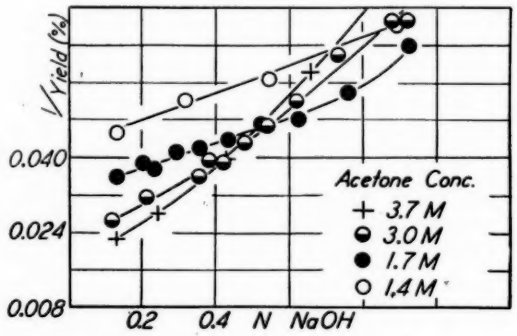


FIG. 3. Reciprocal of alcohol yield plotted against normality of sodium hydroxide. Current density 0.0637 amp./cm².

will be seen that this is approximately true, particularly at the lower concentrations of acetone and NaOH.

Next a series of runs was made to determine the specific effects of the nature of the electrolyte. Some typical results are shown in Fig. 4 which represents runs made in acetone concentrations of 3.0 *M* (in the NaOH and KOH curves) and 3.5 *M* (in the NaCl curve) for various concentrations of these electrolytes. The curves show that the nature of both the anion and the cation affect the yields of both isopropyl alcohol and pinacol. In order to show the cation effect experiments were tried on $Ba(OH)_2$, NaOH, and KOH. In the $Ba(OH)_2$ no reduction of acetone took place, while in KOH the yields of both products were always higher than in the same concentration of NaOH. Thus the reduction of acetone is seen to be furthered by using a more difficultly reducible cation. Replacing the original hydroxyl ion by either sulfate or chloride increased the yield of isopropyl alcohol and lowered the yield of pinacol.

A series of runs was also made to determine the effect of amalgamating the mercury with sodium. In these the deamalgamation process was turned off and the sodium allowed to accumulate in the mercury. As the concentration of the amalgam rose the current yield of both isopropyl alcohol and pinacol rose until at an amalgam which was 0.1 molal in sodium the yield of acetone reduction products was three times what it was on pure mercury. The ratio of pinacol to isopropyl alcohol, however, showed only a very small rise as the amalgam concentration increased.

A number of runs were made in which the concentrations of acetone and electrolyte were held constant and the current density was varied. The results are shown in Figs. 5a–d. The peculiar wavy nature of some of these curves is similar to the effect found by Wilson and Wilson,[5] but it is less pronounced. There seems to be reason to suspect that the waviness could be removed completely by devising better methods of removing the sodium from the mercury. The only general observation which can be made is that decreasing the current density favors the reduction of acetone over that of sodium, the reduction to pinacol being increased more than the reduction to isopropyl alcohol.

Experiments were also tried in which the stirring rate was varied, and others in which air and hydrogen were bubbled through the solution. None of these had any effect on the rate of reduction.

DISCUSSION

Two mechanisms have been advanced to account for the production of isopropyl alcohol and pinacol from acetone. The older theory is that originated by Tafel[1] and most recently advanced by Leslie and Butler.[4] These authors state only that hydrogen atoms are the actual reducing agent. However, the only plausible possibilities based on this assumption are those in which the hydrogen atoms add directly to acetone

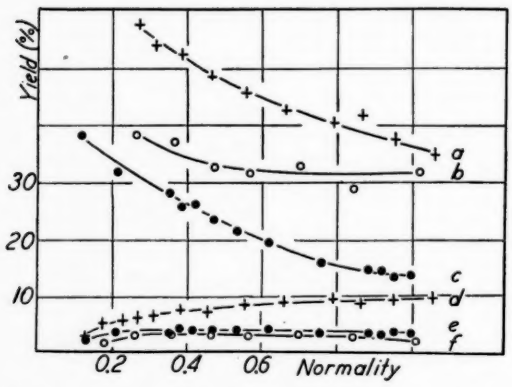
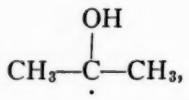
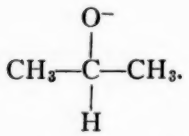


FIG. 4. Yield of alcohol and pinacol plotted against the normality of electrolyte. Current density 0.0637 amp./cm². *a*, alcohol yield in potassium hydroxide, 3.0 *M* acetone. *b*, alcohol yield in sodium chloride, 3.5 *M* acetone. *c*, alcohol yield in sodium hydroxide, 3.0 *M* acetone. *d*, pinacol yield in potassium hydroxide, 3.0 *M* acetone. *e*, pinacol yield in sodium hydroxide, 3.0 *M* acetone. *f*, pinacol yield in sodium chloride, 3.5 *M* acetone.

to form



or



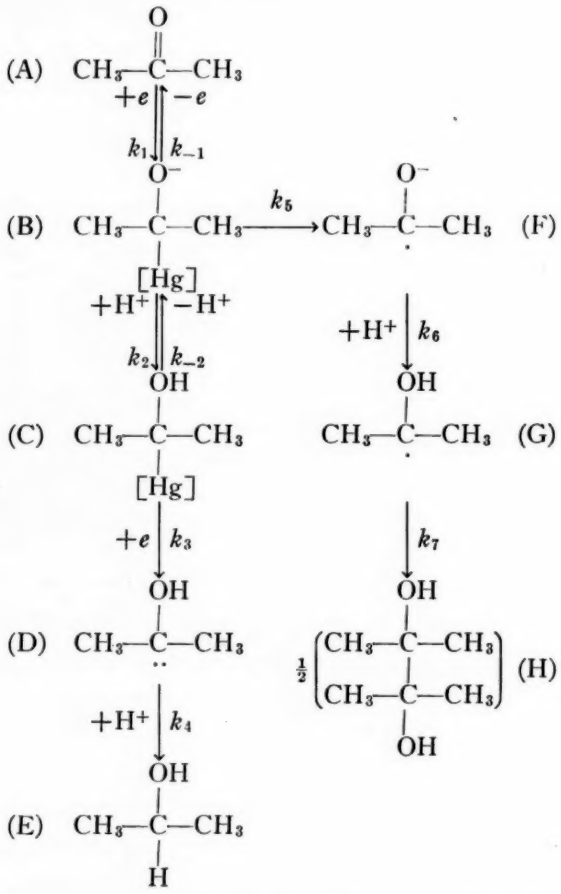
The first of these could dimerize to form pinacol, or produce isopropyl alcohol by reaction with water, e.g., by

$$CH_3COHCH_3+H_2O\rightarrow CH_3CHOH+OH, \quad (5)$$

or by reaction with a second hydrogen atom. However, none of these possibilities gives kinetics which are similar to those observed.

The direct reduction theory of Müller[3] comes closer to the observed facts. However, his mechanism predicts that the pinacol yield should be proportional to the square of the acetone concentration, and does not account for the observed change from this to a linear dependence on acetone concentration. Neither does his mechanism account for the large effect of hydroxyl ion concentration.

However, the following mechanism, which is quite similar in many respects to that of Müller, seems to account for most of the observed phenomena.



The first step in this process (reaction 1) is the attachment of acetone to the mercury surface. The polar character of the C=O group in acetone causes the positive carbon atom to be attracted to the negative mercury surface. A pair of unshared electrons on a mercury atom is donated

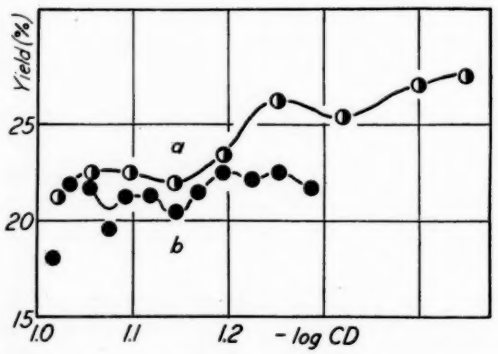


FIG. 5a. Yield of alcohol plotted against the log of the current density. *a*, 3.3 *M* acetone, 0.46 *N* sodium hydroxide. *b*, 3.8 *M* acetone, 0.5 *N* sodium hydroxide.

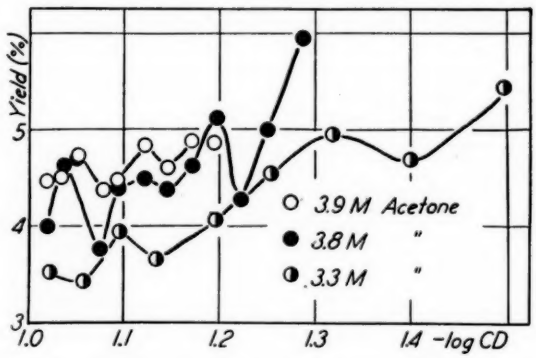


FIG. 5b. Yield of pinacol plotted against the log of the current density in 0.5 *N* sodium hydroxide.

to this carbon atom, forming a covalent bond, and displacing one of the electron pairs of the double bond to the oxygen, giving the oxygen atom a negative charge. This negative oxygen atom is strongly basic, and in the presence of water an acid-base equilibrium is set up (reaction 2). Under the influence of the electric field the acid (C) may ionize away from the surface (reaction 3) to form the carbanion D. This in turn is strongly basic and will capture a proton from water (reaction 4) to form isopropyl alcohol.

If the basic form of the adsorbed acetone (B) dissociates from the surface, it will ordinarily form acetone, but when the surface is sufficiently negative it may form an ion (F) which is simply an acetone molecule with an extra electron (reaction 5). This ion is stabilized to some extent by the resonance between structures

$$CH_3\text{—}\overset{\displaystyle O^-}{\overset{|}{\underset{\cdot\cdot}{C}}}\text{—}CH_3 \rightleftharpoons CH_3\text{—}\overset{\displaystyle \dot{O}}{\overset{|}{\underset{\cdot\cdot}{C}}}\text{—}CH_3. \quad (6)$$

This ion, however, will soon pick up a proton (reaction 6) to form (G), which dimerizes (reaction 7) to form pinacol (H).

It might be thought that (B) could also ionize from the surface to form an ion

$$\left[\begin{array}{c} \cdot\cdot \\ :O: \\ | \\ CH_3\text{—}C\text{—}CH_3 \\ \cdot\cdot \end{array}\right]^{=},$$

but this would violate the adjacent charge rule by having negative charges on two adjacent atoms, and would therefore be very unstable. Likewise, the dissociation of (C) from the surface to form (G) directly is unlikely since the negative charge of the surface no longer aids the reaction, and in any case leads to kinetics which differ from those observed.

In setting up the kinetics of this mechanism a number of points must be observed. In alkaline solutions the protons for reactions 2, 4, and 6 will come from water. In the reverse of reaction 2 the formation of the base (B) will occur only by the reaction with OH^-. The concentration of OH^- involved in this process is not the bulk concentration, but the concentration near the surface, which we shall denote by $[OH^-]_e$. Furthermore, reactions 1 and 3 involve electron transfers from the electrode, and therefore have rates which are affected by the potential of the electrode.

If the rate equations for this mechanism are now set up in the usual way, assuming that a steady state is reached in which the intermediates (B), (C), (D), (F), (G) all have constant concentrations, then the following equations are found for the rates of formation of isopropyl alcohol and pinacol, $I_{\text{alc.}}$ and $I_{\text{pin.}}$:

$$I_{\text{alc.}} = \frac{k_1k_2k_3[A]}{k_3(k_{-1}+k_2+k_5)+k_{-2}(k_{-1}+k_5)[OH^-]_e}, \quad (7)$$

$$I_{\text{pin.}} = \frac{k_1k_5(k_{-2}[OH^-]_e+k_3)[A]}{k_3(k_{-1}+k_2+k_5)+k_{-2}(k_{-1}+k_5)[OH^-]_e}. \quad (8)$$

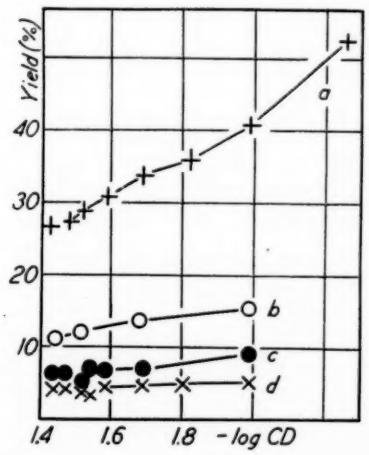


FIG. 5c. Yield of alcohol plotted against the log of the current density. *a*, 0.13 *N* sodium hydroxide, 2.3 *M* acetone. *b*, 0.35 *N* sodium hydroxide, 1.2 *M* acetone. *c*, 0.8 *N* sodium hydroxide, 1.1 *M* acetone. *d*, 1.1 *N* sodium hydroxide, 1.3 *M* acetone.

The rate of the acid-base equilibrium (k_2 and k_{-2}) is much larger than the rate of any of the dissociation reactions (k_{-1}, k_3, k_5) so that these equations may be approximated by the simpler equations

$$I_{\text{alc.}}=\frac{k_1k_2k_3[\text{A}]}{k_3k_2+k_{-2}(k_{-1}+k_5)[\text{OH}^-]_e}, \tag{9}$$

$$I_{\text{pin.}}=\frac{k_1k_5k_{-2}[\text{OH}^-]_e[A]}{k_3k_2+k_{-2}(k_{-1}+k_5)[\text{OH}^-]_e}. \tag{10}$$

Before these equations can be applied an expression must be found for $[\text{OH}^-]_e$ in terms of measurable quantities. An exact treatment of this would be very complicated, but the following argument shows the important features. If no acetone is present, the discharge of Na^+ is controlled by the diffusion of NaOH to the electrode surface, and at the surface itself the NaOH concentration is practically zero. If acetone is present, on the other hand, the reduction produces OH^-, and the current of OH^- from the surface together with the current of Na^+ to the surface produces an ordinary transport process with no necessity of diffusion if the Na^+ current and the OH^- current are in the proper ratio. Under these circumstances the OH^- concentration would be equal to the bulk concentration right up to the electrode surface. In these experiments the situation is intermediate. The acetone reduction current is present, but the OH^- produced is not sufficient to eliminate the diffusion completely. Hence the OH^- concentration at the electrode is less than in the bulk of the electrolyte, but not zero.

In the most dilute acetone solutions, the OH^- concentration near the electrode is nearly zero, and one would expect the small deviation from zero to be proportional to the acetone current. Since this is owing mainly to the formation of isopropyl alcohol, it leads to a proportionality between the value of OH^-_e and the acetone concentration. If we put $[\text{OH}^-]_e=b[A]$, the equations for $I_{\text{alc.}}$ and $I_{\text{pin.}}$ in dilute solutions become

$$I_{\text{alc.}}=\frac{k_1k_2k_3[A]}{k_3k_2+k_{-2}(k_{-1}+k_5)b[A]}, \tag{11}$$

$$I_{\text{pin.}}=\frac{k_1k_5k_{-2}b[A]^2}{k_3k_2+k_{-2}(k_{-1}+k_5)b[A]}. \tag{12}$$

We thus obtain results in agreement with the observed proportionality between $I_{\text{alc.}}$ and the acetone concentration and $I_{\text{pin.}}$ and the square of the acetone concentration.

In the more concentrated solutions the OH^- concentration is not reduced very much near the electrode, and we may assume that the value of $[\text{OH}^-]_e$ is approximately equal to the bulk concentration. Under these assumptions

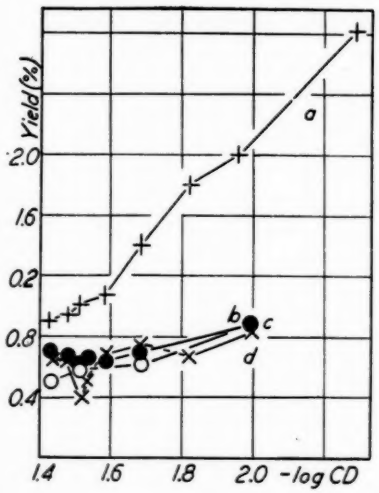


FIG. 5d. Yield of pinacol plotted against the log of the current density. *a*, 0.13 *N* sodium hydroxide, 2.3 *M* acetone. *b*, 0.8 *N* sodium hydroxide, 1.1 *M* acetone. *c*, 0.35 *N* sodium hydroxide, 1.2 *M* acetone. *d*, 1.1 *N* sodium hydroxide, 1.3 *M* acetone.

$$I_{\text{alc.}}=\frac{k_1k_2k_3[A]}{k_3k_2+k_{-2}(k_{-1}+k_5)[\text{OH}^-]}, \tag{13}$$

$$I_{\text{pin.}}=\frac{k_1k_5k_{-2}[\text{OH}^-][A]}{k_3k_2+k_{-2}(k_{-1}+k_5)[\text{OH}^-]}. \tag{14}$$

Thus both $I_{\text{alc.}}$ and $I_{\text{pin.}}$ should become proportional to the acetone concentration. This accounts for the straightening out of the plot of $I_{\text{pin.}}$ against acetone concentration.

These same equations predict that in all but the most dilute acetone solutions, the reciprocals of $I_{\text{alc.}}$ and $I_{\text{pin.}}$ should be linear functions of $[\text{OH}^-]$, which is in approximate agreement with the observations. They also explain why increasing the concentration of OH^- decreases the yield of isopropyl alcohol and increases the yield of pinacol.

These equations do not explain the leveling off of the plot of $I_{alc.}$ against acetone concentration. This may be owing to the fact that the solutions are nearing saturation. In this region an increase in concentration of acetone does not necessarily mean a corresponding increase in the activity of acetone. It would be interesting to plot these currents as functions of acetone activity rather than concentration, but the necessary data are not available.

The effect of substituting other negative ions for OH^- is explained by the fact that the concentration of OH^- affects the equilibrium of reaction 2. The effects are all in the direction predicted by this mechanism, but cannot be explained quantitatively because of the difficulty of analyzing the complex diffusion-conduction systems set up near the electrode in these systems.

The effect of changing the cation is tied up with the fact that such charges affect the electrode potential quite strongly. In the Ba^{++} solutions the potential necessary to reduce Ba^{++} is below that necessary to reduce the acetone. In K^+ the electrode is more negative than in Na^+. As a result k_1 and k_3 are increased, while k_{-1} is decreased. This results in an increase in the values of both $I_{alc.}$ and $I_{pin.}$.

The effect of current density is similar. At higher current densities the electrode is made more negative. This increases $I_{alc.}$ and $I_{pin.}$ and also the sodium current. In the discharge of Na^+ the whole of the electrode potential assists the discharge rate, but in the reduction of acetone on the surface the electrons do not immediately pass all the way through the electrical double layer. In reaction 1 the reduction electron moves only from the metal to the oxygen atom, and is completely removed from the surface only by reaction 3 or reaction 5. Thus the effect of the electrode potential is divided between the two steps. Because of this none of the k's is increased as rapidly as the sodium current, and hence it is easily seen that the increase in $I_{alc.}$ and $I_{pin.}$ is less than the increase in sodium current. The fraction of the current going into the reduction of acetone is decreased by increasing the current density.

The ratio $I_{pin.}/I_{alc.}$, which is given by

$$\frac{I_{pin.}}{I_{alc.}}=\frac{k_5k_{-2}[OH^-]_e}{k_2k_3}, \tag{15}$$

is affected by the electrode potential only through k_3. Hence we would expect an increase in current density to decrease this ratio, which again is in agreement with experiment. This is also in agreement with the prediction of Semerano[10] that at very low current densities only pinacol would be formed.

[10] G. Semerano, Gazz. chim. ital. **62**, 959 (1932).

Letter to the Editor

PROMPT publication of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is the third of the month. Because of the late closing date for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not in general exceed 600 words in length.

Crystal Luminescence—Paramagnetic Ions as Centers

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September 21, 1944

IN a previous communication,[1] after considering the polarization of luminescence of ruby, it was stated that a general interpretation of crystal luminescence based on the following concept could be attempted: "The absence or existence of luminescence is conditioned by the complete quenching of the orbital moment (caused by crystalline fields) of a possible center or its conservation along one or more directions within the crystal."

Among the luminescent solids which give discrete or line spectra are those in which paramagnetic ions act as centers of luminescence. Below are given some facts regarding the luminescence of this class of crystals, which support the above concept.

(1) It is now well known that the sharp-line luminescence of either pure rare-earth salts or solids containing rare earths as impurities, arises from the transitions within the shielded incomplete $4f$ shell of the rare-earth ion. The effect of this shielding from the surrounding fields is to leave the orbital moment of the ion free to orient in a magnetic field, like a paramagnetic gaseous atom. This is reflected in luminescence as the ease with which the rare-earth ions take up positions[2] as luminescent centers in any crystalline matrix. Without regard to the structure of the surrounding matrix, the ion remains a center of sharp-line luminescence, as there is no quenching of the orbital angular momentum along any direction within the crystal. There is thus no directional fixation of the L moment of the ion owing to surrounding fields.

(2) Solids activated by ions of the transition elements give discrete spectra arising from transitions owing to the rearrangement of electrons in the incomplete $3d$ shell. Trivalent Cr^{+++} and divalent Mn^{++} ions will be considered here as representatives. In the case of phosphors activated by chromium, it is found[3] that the Cr^{+++} ion acts as a luminescent center only where Cr_2O_3 can be isomorphous with the crystalline matrix in which it is embedded. The Cr^{+++} ion, which then can be shown to occupy a definite position[4] in the lattice of the matrix crystal, will have its orbital angular momentum conserved along one or more definite directions, depending on the symmetry of the surrounding fields and will then be in a condition to be excited and to luminesce. If it is embedded anyhow in a matrix, not isomorphous with Cr_2O_3, the ion, being subject to totally unsymmetrical[5] fields, will have its orbital moment completely quenched and there will be no luminescence. Conservation of the L moment along a single definite axis of symmetry of the crystal will result in polarization of luminescence, which in the case of corundum has already been referred to.[1]

Manganese, on the other hand, i.e., Mn^{++} ion, enters a wide variety of crystal matrices as an impurity and remains luminescent. Randall[6] has shown it to luminesce in pure halide crystals as well as in ZnS, $MgSO_4$, $MgSiO_3$, $Cd_2B_2O_5$, etc. The Mn^{++} ion having $3d^5\ {}^6S$ as the basic term is in the S state and has therefore little orbital interaction with the surrounding fields. There is no quenching effect caused by the fields and the ion is in a position to be excited and to luminesce within matrices of varied structures.

(3) The observations of Rupp[6] on the partial polarization of luminescent light, perpendicular to an applied magnetic field, of ZnS phosphors, activated by Mn and Cu ions, are also significant. This shows that the paramagnetic ions are comparatively free to orient in a magnetic field, the effect being greater for Mn—an ion of greater magnetic moment. Riehl[7] has shown that the activating atoms are "mobile" within the ZnS lattice and that there is sufficient space for the ion within the unoccupied tetrahedra (with S atoms at corners) the interlinking of which gives the ZnS lattice. The freedom to orient and the mobility of the ion mean that there is feeble interaction of the L moment with the crystal fields and that there is no quenching effect. This is then accompanied by luminescence.

It is seen from the above cases of crystal luminescence caused by paramagnetic ions as centers that the interaction of the orbital moment and the surrounding fields has to be considered, the existence of luminescence being conditioned by the conservation of the orbital angular momentum along one or more directions within the crystal.

[1] B. V. Thosar, J. Chem. Phys. **10**, 246 (1942).
[2] Tomaschek, Trans. Faraday Soc. **35**, 148 (1939).
[3] Deutschbein, Physik. Zeits. **33**, 874 (1932).
[4] B. V. Thosar, Phil. Mag. **26**, 878 (1938).
[5] Van Vleck, *Theory of Electric and Magnetic Susceptibility* (Oxford University Press, 1932), p. 288.
[6] Rupp, Ann. d. Physik **75**, 326 (1924).
[7] Riehl, Trans. Faraday Soc. **35**, 135 (1939).